

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 1995	3. REPORT TYPE AND DATES COVERED Final Report	
4. TITLE AND SUBTITLE Laser Induced Chemical Vapor Deposition of Thin Films			5. FUNDING NUMBERS F6170894C0002	
6. AUTHOR(S) Dr Joseph Zahavi				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Technion Technion City Haifa 32000 Israel			8. PERFORMING ORGANIZATION REPORT NUMBER N/A	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) EOARD PSC 802 BOX 14 FPO 09499-0200			10. SPONSORING/MONITORING AGENCY REPORT NUMBER SPC 94-4006	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE A	
13. ABSTRACT (Maximum 200 words) This report results from a contract tasking Technion as follows: Investigate the characteristics of thin silicon nitride films deposited on substrates via the use of chemical laser deposition techniques.				
14. SUBJECT TERMS Nil			15. NUMBER OF PAGES 50	
			16. PRICE CODE N/A	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102



LASER INDUCED CHEMICAL VAPOR DEPOSITION OF THIN FILMS

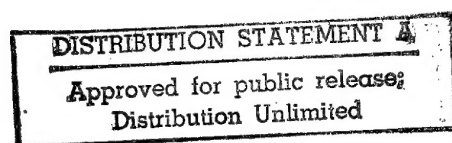
ANNUAL REPORT (1-12/94)

CONTRACT NO. F61708-94-C0002

Submitted by

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Haifa, Israel

DTIC QUALITY INSPECTED



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CONTENT

1. INTRODUCTION

2. EXPERIMENTAL

2.1 List of experiments for silicon nitride deposition

2.2 Methods of analyses

2.3 Experiment for silicon carbide deposition

3. RESULTS AND DISCUSSION

3.1 Characterization of Silicon Nitride Films

3.1.1 Films Composition

3.1.2 Film Thickness and Refractive index

3.1.3 Microstructure

3.2 Absorption Measurements of Acetylene by Excimer Laser

3.3 Gas analysis

3.3.1 Silicon Nitride Deposition

4. SUMMARY

Appendix A: Progress report no.1

Appendix B: Progress report no.2

Appendix C: List of measurements of molecular partial pressure during experiments

INTRODUCTION

This report summarized the research activities during the first year of work as was planned in the proposal. It completes the information which was given in the previous two progress reports. Basically, the aim of the first year was to study the possibility of deposition of silicon nitride thin films from silane and ammonia at low temperatures. The investigation was carried out by studying the effect of substrate temperature on deposition rate and film quality. In addition, the photochemical reaction was studied by analyzing the composition of gas molecules prior and during laser irradiation.

At the end of the first year it was also possible to start doing experiments for deposition of silicon carbide from silane and acetylene.

EXPERIMENTAL

2.1 List of Experiments For Silicon Nitride Deposition

Table 1 lists the deposition conditions for the formation of silicon nitride thin films. The table includes deposition temperature, gas flow rate, total pressure, laser energy, repetition rate and number of pulses. As can be observed from this table the gas mixture was changed during experiments in order to continue optimization of the deposition process. The flow of Ar into the chamber was necessary for washing the window in order to prevent deposition on it. The repetition rate was constant in all the experiments, except run SIN36. The laser energy was changed in the range of 130-210 mJ/p. The changes in the laser energy were uncontrollable due to degradation in the laser performance. The pressure values are given as total pressure including the washing gas which

contributed the major part to the value of the total pressure. In addition to the parameters which are specified in the table, it should be mentioned that the base vacuum prior to deposition was $1 \cdot 10^{-6}$ Torr. The substrate on which the deposition was carried out was Si(100) for experiments SIN30-SIN36 and SiO₂ (55 thick)/Si(100) in experiments SIN40-SIN47.

2.2 METHODS OF ANALYSES

The investigation and optimization of the process of SIN film deposition was carried out by monitoring the various parameters which affect the deposition rate and film properties. These parameters are total pressure, gas flow rate, substrate temperature, laser energy, laser repetition rate and number of pulses. There was also a special need to maintain a constant distance between the laser beam and the substrate.

During each experiment the value of these parameters were recorded and also a gas analyses was done several times and the different kind of molecules and radicals which were formed during laser irradiation were determined.

The quality of the films was characterized by examining their composition by Auger Electron Spectroscopy (AES) and SIMS and the microstructure was examined by using Transmission Electron Microscopy (TEM). The thickness of the film was measured mainly by ellipsometry however sometime we had difficulties which arised from the fact that the refractive index of the substrate was different from the Si standard which was used to calibrate the instrument. Few measurements of the refractive index were peformed by making tranmittance and reflectance measurements and calculating the refractive index from the minima or maxima of theses curves.

Table 1: Deposition conditions of LCVD experiments

EXP.ID	TEM. °C	FLOW RATE SCCM			PRESS. Torr	LASER BEAM		
		SiH4	NH3	Ar		INT. mJ/p	R.R Hz	No. Pulses
SIN30	400*	25	7.5	105	5.9	190	20	50000
SIN31	300*	25	7.5	100	6.4	210	20	50000
SIN32	200*	25	7.5	100	6.5	210	20	50000
SIN33	250*	25	7.5	100	5.8	150	20	32000
SIN34	250*	25	7.5	100	6.5	200	20	50010
SIN35	200*	25	7.5	100	6.3	170-130	20	50003
SIN36	200*	25	7.5	100	6.1	170	5	30012
SIN37	300*	15	25	50	4.7	130	20	16000
SIN38	220*	10	15	100	6	130	20	20010
SIN39	280*	15	25	50	5.4	135	20	10000
SIN40	300*	15	25	50	5.5	150	20	10000
SIN41	320*	15	25	50	4.8	160	20	40007
SIN42	270*	15	25	50	5.0	150	20	40177
SIN43	220*	15	25	50	4.8	150	20	40000
SIN44	220*	9	15	100	6.0	150	20	40164
SIN45	170**	9	15	100	5.8	150	20	40008
SIN46	120**	9	15	100	6.0	150	20	40003
SIN47	120*	9	15	100	6	150	20	92500
SIN48	315*	9	15	100	6	130	20	100200
SIN49	200*	9	15	100	6	110	20	100000

*The temperature was measured on the substrate surface

** The temperature was measured on the specimen holder which is expected to be higher than the substrate temperature

2.3 Experiments for Silicon Carbide Deposition

The major part of the work for LCVD of SIC concentrated in the installation of acethylene line for supplying the precursor gases needed to SIC formation. In addition, absorbtion measurements were conducted by measuring the incident laser intensity and the intensity after travelling through the chamber in a vacuum and at several pressures.

3. RESULTS

3.1 Characterization of Silicon Nitride Films

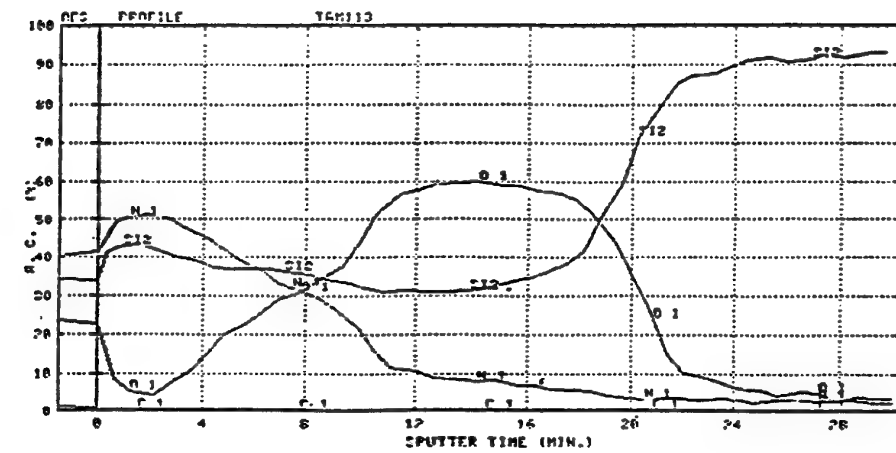
3.1.1 Films Composition

The depth composition profiles of the silicon nitride films obtained in experiments SIN30-36 were discussed in the progress report No.2 (App.B). These results which were obtained at SiH_4/NH_3 ratio of 10/3 showed that the composition of the films depended upon deposition temperature and the Si/N atomic ratio was changed in the range of 0.55-1, while both stoichiometric silicon nitride (Si_3N_4) and silicon nitride films which are obtained at low pressure CVD have a ratio of 0.75. No correlation could be observed between the Si/N ratio between the temperature and film composition. The film which has a Si/N ratio close to the stoichiometric silicon nitride was obtained at a substrate temperature of 250°C. An important result that is shown in the depth composition is that there is high amount of oxygen in the films which were obtained at substrate temperature of about 300°C and lower. This new factor must be considered in studying the deposition at low temperature. Fig.1 shows a depth profile composition of silicon nitride films obtained at another sery of experiments. In these experiments the flow

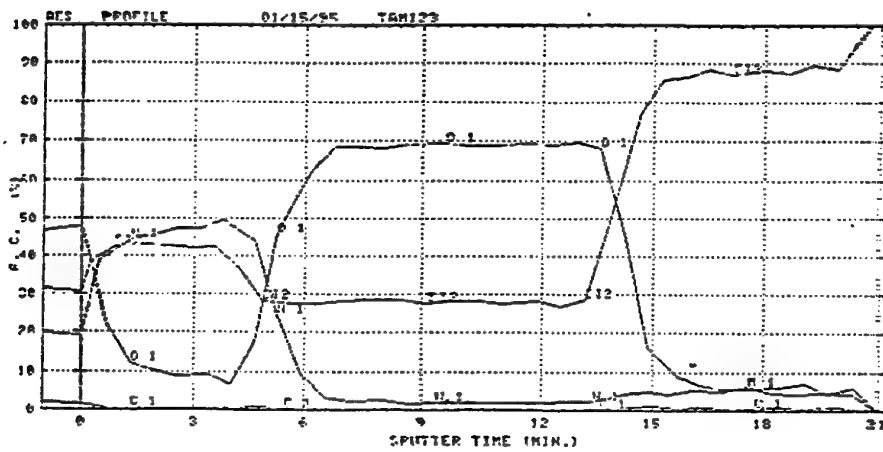
rate of the precursor gas was decreased keeping SiH_4/NH_3 ratio of 3/5. The reason for lowering the amount of the silane and increasing ammonia was to prevent powder formation in the gas phase due to the interaction between silane derivative which might be produced due to silane decomposition by the laser beam.

The AES depth composition profiles show (e.g Fig.2) that at all temperatures which were examined the composition is homogenous with a constant Si/N atomic ratio of between 0.8 and 0.9. The interface between the silicon nitride film and the silicon oxide substrate is very sharp. The film thickness decreases with lowering temperature, starting at 50 nm at 320°C (SIN41) followed by 30 nm at 220°C (SIN44) ending at 20 nm at 170°C* (SIN45) (the deposition conditions are summarized in table 1). The AES measurement performed on SIN42 specimen was unsuccessful probably due to the presence of trapped gas bubbles inside the film.

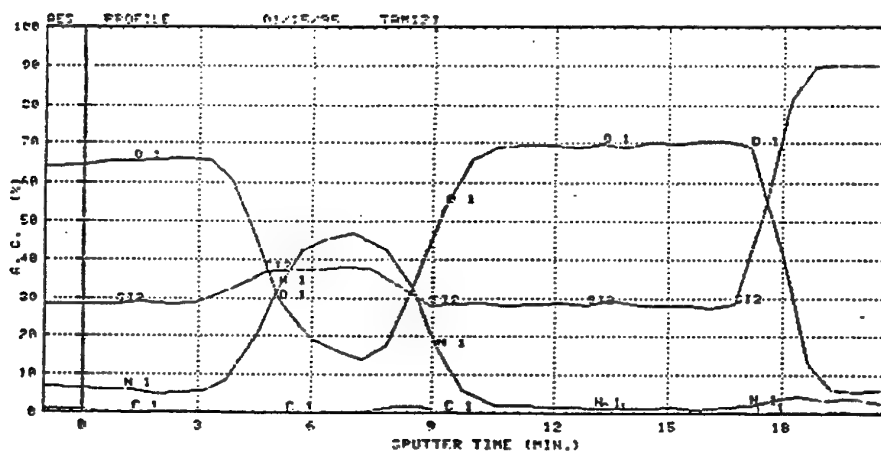
SIMS composition depth profiles of the specimen prepared at 320°C (SIN41-Fig.3a) show uniform composition along the whole thickness of the silicon nitride film. the thickness of the film is about 50 nm, the same as obtained by AES measurement profile. In addition to Si and N one can see low concentration of impurities such as carbon, hydrogen (as OH) and oxygen. At the interface between the silicon nitride and silicon oxide the carbon and OH concentration increase in about one order of magnitude probably due to residual alcohol which was used to clean the substrate before inserting it into the vacuum chamber. The SIMS profile of specimen SIN42 which was prepared at 270°C (Fig.3b) also show uniform composition, however the relative concentration of the hydrogen is higher than that observed in specimen SIN41. According to these profiles the film thickness is about 100 nm. In specimen SIN44 prepared at 220°C (Fig.3c) the thickness is of about 20 nm and there is a slight variation in composition at the middle of the film depth. In addition, the oxygen concentration is much higher than the



a



b



c

Fig1. AES depth composition profile of the silicon nitride/silicon oxide specimens prepared according to experiments: a) SIN41, b) SIN44, c) SIN45 (see table 1)

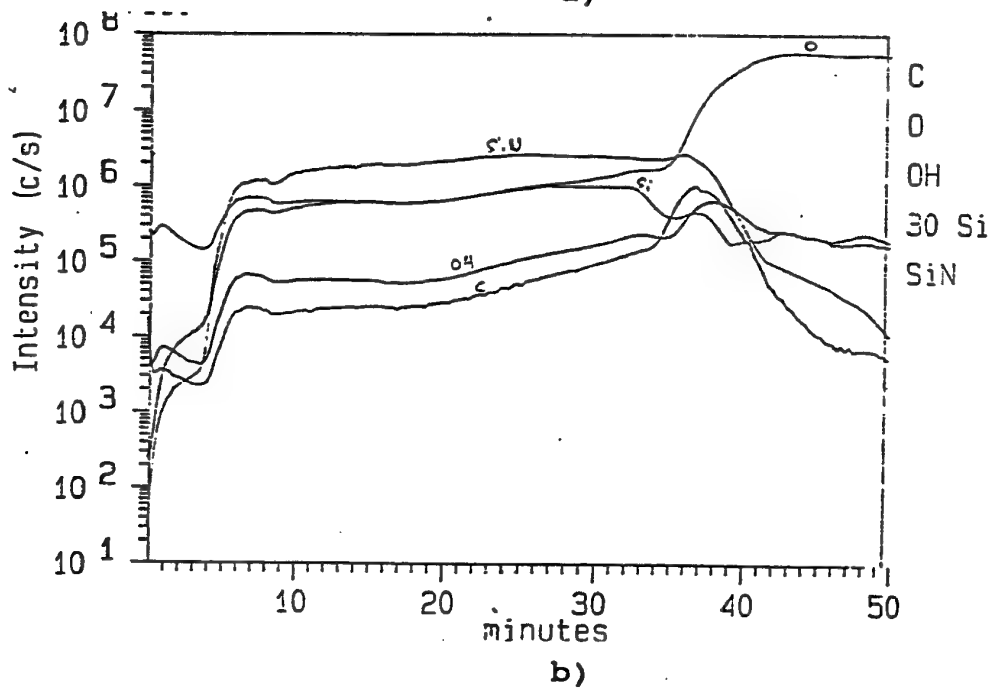
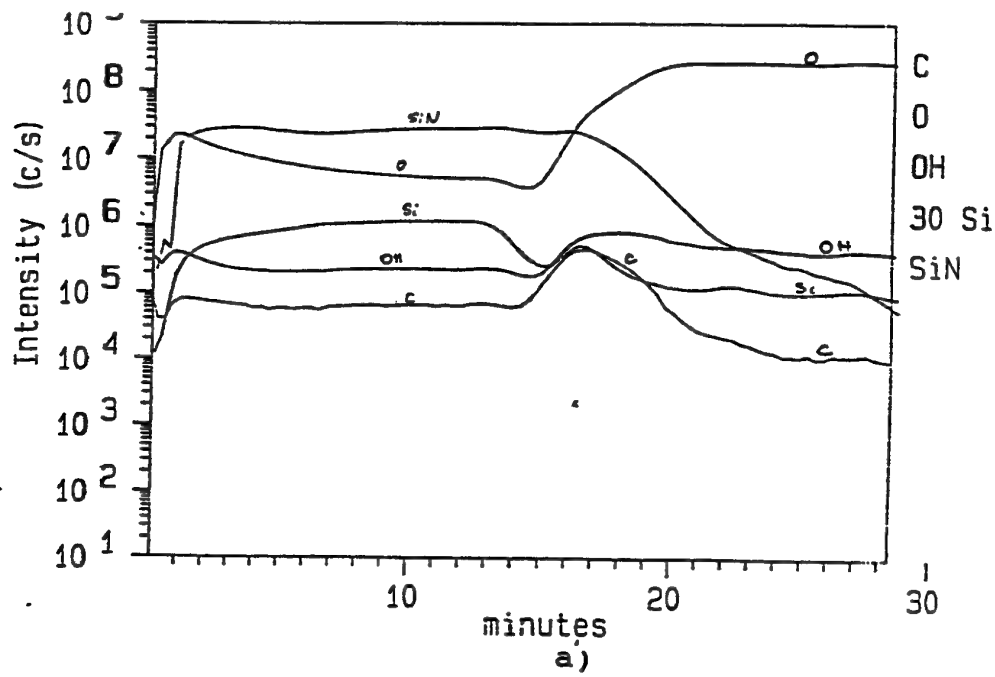


Fig. 3: SIMS composition depth profile of the silicon nitride films deposited on SiO_2/Si substrate at :a) 320°C b) 270°C

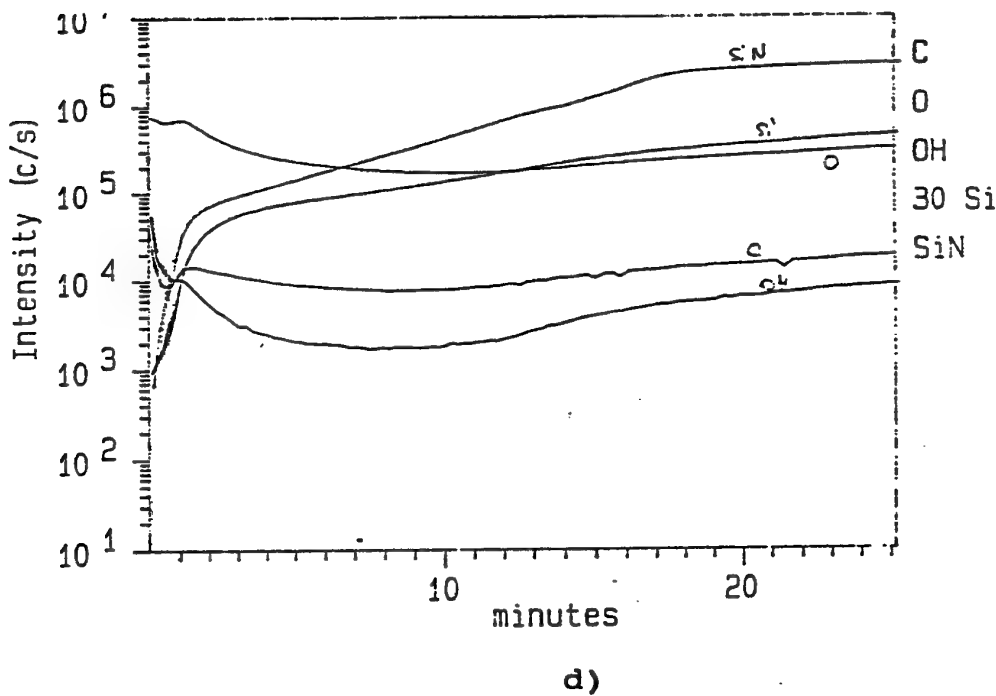
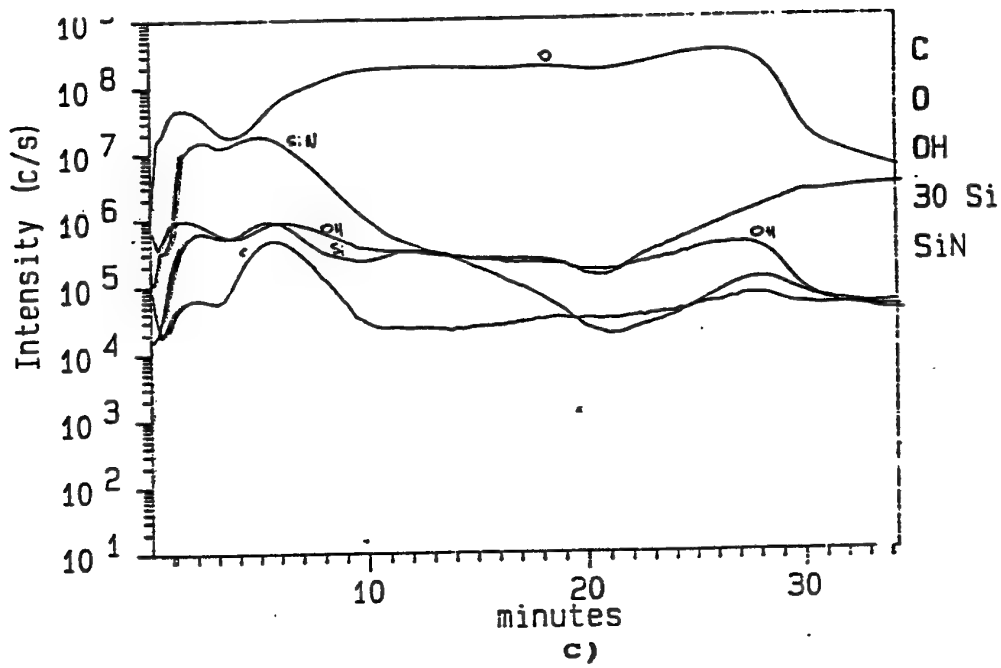


Fig. 3 (cont'): SIMS composition depth profile of the silicon nitride films deposited on SiO₂/Si substrate at :c) 220°C d) LCVD silicon nitride (reference specimen)

concentrations of all the other elements including silicon and nitrogen. This result is in contradiction to the AES depth profile. Fig 3d shows a SIMS depth profile of silicon nitride film prepared by Low Pressure CVD (LPCVD) which was used as a reference to our Laser CVD specimens.

3.1.2 Thickness and Refractive index of Silicon Nitride Films

The results of thickness and refractive index measurements for films obtained in runs SIN30-SIN 36 were presented in progress report No.2 (APP.B). The results for runs SIN41-SIN49 are listed in table No.2. These results were obtained either by ellipsometry or by recording transmittance and reflectance spectra in the range of 400-900 nm and calculating the refractive index from the 1/4 which correspond to maximum of reflectance shown in the curve. This type of measurement could be carried out for the films obtained in runs SIN47-SIN49 where the deposition time was twice the time for the other experiments and therefore, the thickness was relatively high so that it was possible to get the maxima in the reflectance curve. It should be

Table 2: Thickness and refractive of silicon nitride films

EXP. ID	Temp. (°C)	No.Pulses	Thick. (nm)	Ref.Ind n
SIN41	320	40007	60	1.98
SIN42	270	40177	130	1.80
SIN43	220	40000	6.5	1.75
SIN44	220	40164	33	1.90
SIN45	170	40008	82	1.75
SIN48	315	100200	208	1.94
SIN49	200	100000	290	1.82

emphasize that we tried to measure all specimens ellipsometry however it was not possible to get results for all the samples due to the limitation of instrument to make calculation based on and of the polarized light which might be in a region where there is not exact solution for the ellipsometric equations.

3.1.3 Microstructure

Fig. 4 shows TEM micrographs of a vertical view of a cross section of SIN film obtained in experiment SIN34. One can observe that the film contains voids which have to be eliminated in order to get an homogenous film. However it should be noted that these void didn't show any negative effect on the refractive index which was measured (App.B) to be in the range of 2-2.21. Looking at picture 4b which is a magnification of fig.4a one can clearly observe a sharp interface SIN/Si which means that no interaction occurred between the substrate and the deposited film. This result was verified in the AES profile of this film. The estimated thickness from the cross section picture is 125 nm and its value is close to the value of 120 nm found by AES, but it is higher than was measured by ellipsometry (About 105 nm-app.b). Figs 4c and 4d are electron diffraction taken from the cross section. Fig.1c is a selected area pattern taken from the SIN film. As is expected from the deposition conditions the SIN is amorphous and therefore exhibits diffusion rings. The few spots shown in this figure belong to the silicon substrate. A microdiffraction pattern taken from the interface SIN/Si (fig.4d) shows the diffusion rings which are characteristics of the SIN film together with discrete spots of the silicon single crystal substrate.



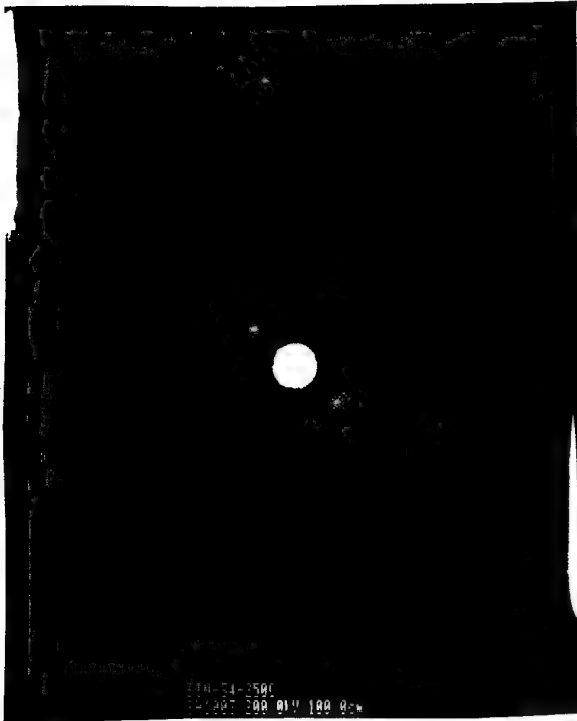
A



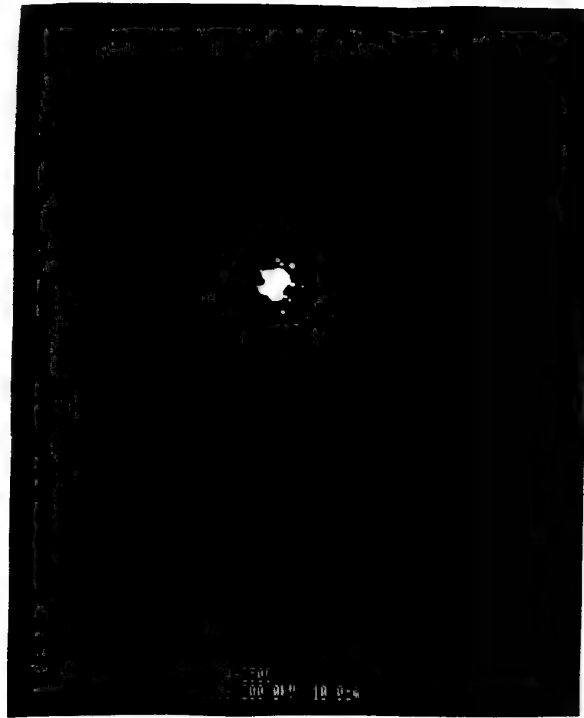
B

Fig.4 : TEM micrographs and diffraction patterns of SIN film deposited at 250°C (run SIN34)

A)*200000 b)*300000 c) Diffraction pattern of SIN film
d) microdiffraction pattern of SIN/SI interface



c



d

Fig.4: (cont')

3.2 Absorption Measurements of Acetylene

Table 3 lists the results of absorption measurements of acetylene gas by using excimer laser (193 nm). The table contains the average intensity as measured by a calorimetric detector while the laser was operated at repetition rate of 10 Hz. It is assumed that the repetition rate does not affect the gas absorption. As can be seen the table includes also the laser energy for one pulse which is measured directly at the laser equipment. The laser intensity was measured at the back of the chamber in order to subtract the absorption of the windows. The incident laser intensity was therefore, measured also at the exit from the chamber while it was in a vacuum. The intensity measurements were carried at several different pressures. The first row can be used as the incident intensity for the measurement in row number 2. However, due to deposition on the chamber windows the apparent incident energy used for the next measurement was measured again and its value is given in row 3. This incident intensity was not changed further during the following absorption measurements probably, because the film thickness on the window remained constant. It is clearly observed from these measurements that the acetylene gas is highly absorbing the laser beam at this wavelength and therefore, it is suitable precursor gas for the formation of silicon carbide.

Table 3: Absorption measurements of acetylene by excimer laser

Gas Pressure (Torr)	Laser Energy (mJ/p)	Laser Intensity (Watt)
0.01	130	0.75
2.0	130	0.55
0.01	130	0.55
2.0	135	0.40
2.8	135	0.30
0.01	130	0.5
4.9(Ar)	130	0.5

3.3 Gas Analysis

3.3.1 Silicon Nitride Deposition

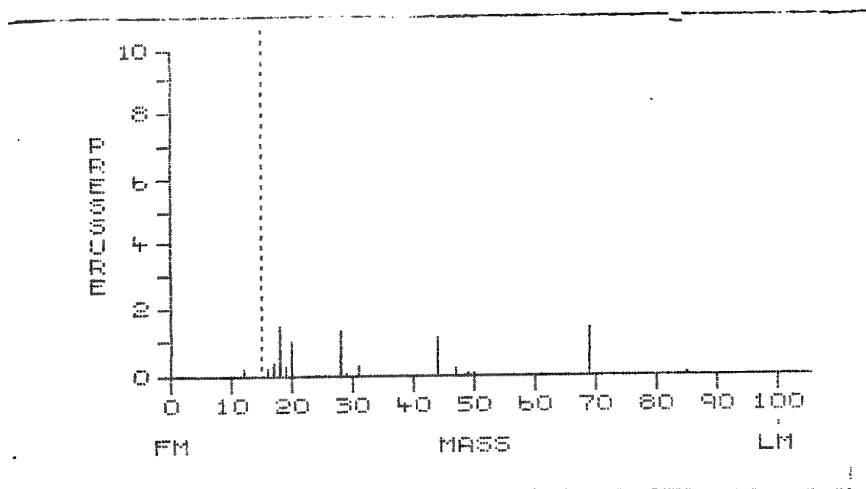
Figs. 5-8 are the data obtained for gas analysis during experiment SIN49. These are examples for the data obtained during each experiment. The composition of gas molecules and their derivatives were recorded in two forms, one form contains information about molecules which have a molecular mass in the range of 1-100 (Fig.5a) and at a second form where only eight different masses can be monitored (Fig.5b). The information data which is obtained in the second mode has the advantage that it contains the partial pressure of each one of eight selected molecules and it is better used to make

quantitative analysis of the gas and gas mixture. The data of this type of results was used to determine the effect of laser intensity, NH_3/SiH_4 ratio and number of pulses, on the type and concentration of gas molecules in the deposition chamber. The data in fig. 5 shows the types gas molecules which were presented in the vacuum system of the spectramass instrument. This result is used as a background to the gas analysis which is carried out at the deposition chamber. Fig. 6 shows the data on gas composition in the deposition chamber while it was evacuated to $1 \cdot 10^{-6}$ Torr.

Looking at the data on gas analysis prior to deposition show that there is a relatively high amount of molecules having mass number 18 and 20. This result must be eliminate, however the source of these molecules is the spectramass which is evacuated by diffusion pump, in contrast to the deposition chamber which is evacuated by a turbomolecular pump.

Fig.7 and fig. 8 show the data analysis of the gas molecules in the chamber before and during deposition, respectively. The data on fig.7a and fig.8a show that there is additional molecules resulting from the NH_3/SiH_4 gas mixture. The peaks at mass numbers of 16 and 17 correspond to NH_2 and NH_3 , respectively. The mass numbers of between 28-32 correspond to SiH_4 and its derivatives. It should be noted that the derivatives of ammonia and silane are presented even without laser irradiation due to the detection mechanism of the spectramass which is based upon cracking of the molecules by using of a filament. Therefore, in order to determine the amount of either silane or ammonia one must sum the amount of all the molecules and their derivatives. The partial pressure of the selected molecules is written in the tables of fig.7b and fig.8b. One can see that the concentration of the molecule which has mass of 16 is increased during laser irradiation, while molecules having molecular mass of 18 and 20 do not change. The molecular mass of 16 is contributed to NH_2 which is produced by laser decomposition of the NH_3 . It should be noted that the the right way for comparing the

concentration data is after normalizing the partial pressure of each molecule to the total partial pressure of all molecules which exist in order to prevent a mistake due to changes in total pressure during each experiment.



a

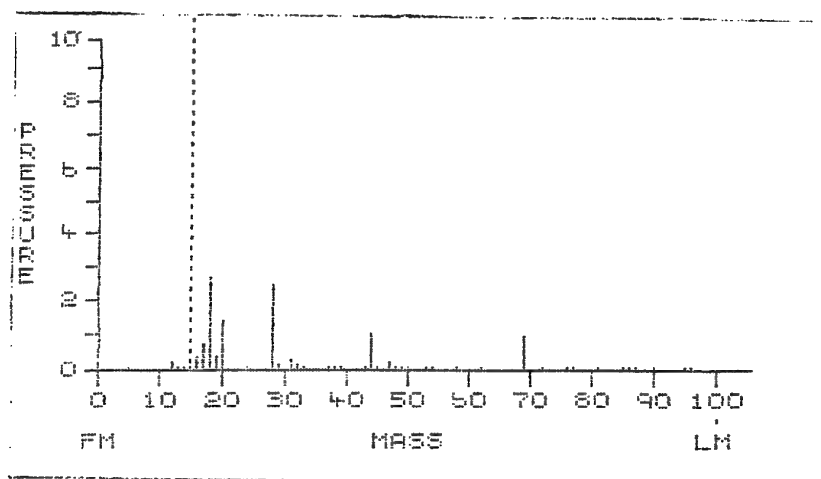
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10.00-10.00	21	OFF	0.000000	0
10.00-10.00	23	OFF	0.000000	0
10.00-10.00	25	OFF	0.000000	0
10.00-10.00	27	OFF	0.000000	0
10.00-10.00	29	OFF	0.000000	0
10.00-10.00	31	OFF	0.000000	0
10.00-10.00	33	OFF	0.000000	0
10.00-10.00	35	OFF	0.000000	0
10.00-10.00	37	OFF	0.000000	0
10.00-10.00	39	OFF	0.000000	0
10.00-10.00	41	OFF	0.000000	0
10.00-10.00	43	OFF	0.000000	0
10.00-10.00	45	OFF	0.000000	0
10.00-10.00	47	OFF	0.000000	0
10.00-10.00	49	OFF	0.000000	0
10.00-10.00	51	OFF	0.000000	0
10.00-10.00	53	OFF	0.000000	0
10.00-10.00	55	OFF	0.000000	0
10.00-10.00	57	OFF	0.000000	0
10.00-10.00	59	OFF	0.000000	0
10.00-10.00	61	OFF	0.000000	0
10.00-10.00	63	OFF	0.000000	0
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10.00-10.00	67	OFF	0.000000	0
10.00-10.00	69	OFF	0.000000	0
10.00-10.00	71	OFF	0.000000	0
10.00-10.00	73	OFF	0.000000	0
10.00-10.00	75	OFF	0.000000	0
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10.00-10.00	81	OFF	0.000000	0
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10.00-10.00	85	OFF	0.000000	0
10.00-10.00	87	OFF	0.000000	0
10.00-10.00	89	OFF	0.000000	0
10.00-10.00	91	OFF	0.000000	0
10.00-10.00	93	OFF	0.000000	0
10.00-10.00	95	OFF	0.000000	0
10.00-10.00	97	OFF	0.000000	0
10.00-10.00	99	OFF	0.000000	0

b

Fig.5: Molecular composition detected by mass quadrupole in the vacuum system of the spectramass instrument(SIN49)

a) Complete data in the molecular mass range 1-100.

b) Partial pressure of 8 selected masses



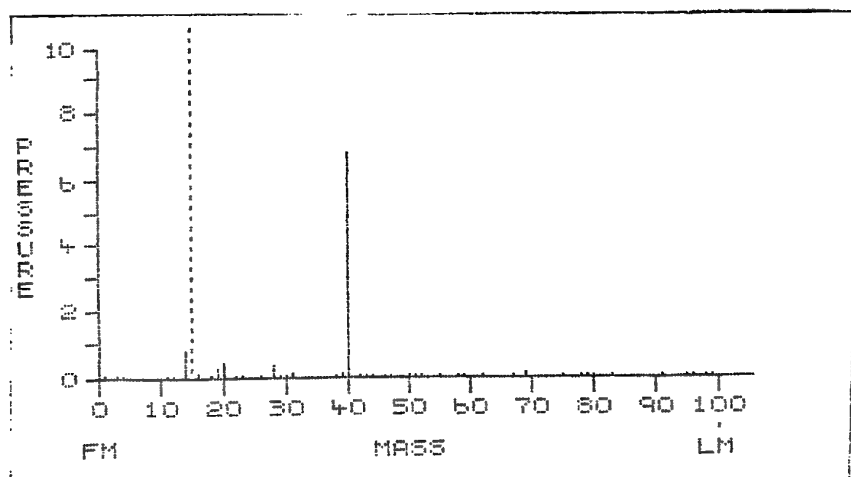
a

CHANNEL	MASS	ALARM	TORR	M/F
1	15	OFF	1.5	1
2	17	OFF	1.5	1
3	19	OFF	1.5	1
4	21	OFF	1.5	1
5	23	OFF	1.5	1
6	25	OFF	1.5	1
7	27	OFF	1.5	1
8	29	OFF	1.5	1
9	31	OFF	1.5	1
10	33	OFF	1.5	1
11	35	OFF	1.5	1
12	37	OFF	1.5	1
13	39	OFF	1.5	1
14	41	OFF	1.5	1
15	43	OFF	1.5	1
16	45	OFF	1.5	1
17	47	OFF	1.5	1
18	49	OFF	1.5	1
19	51	OFF	1.5	1
20	53	OFF	1.5	1
21	55	OFF	1.5	1
22	57	OFF	1.5	1
23	59	OFF	1.5	1
24	61	OFF	1.5	1
25	63	OFF	1.5	1
26	65	OFF	1.5	1
27	67	OFF	1.5	1
28	69	OFF	1.5	1
29	71	OFF	1.5	1
30	73	OFF	1.5	1
31	75	OFF	1.5	1
32	77	OFF	1.5	1
33	79	OFF	1.5	1
34	81	OFF	1.5	1
35	83	OFF	1.5	1
36	85	OFF	1.5	1
37	87	OFF	1.5	1
38	89	OFF	1.5	1
39	91	OFF	1.5	1
40	93	OFF	1.5	1
41	95	OFF	1.5	1
42	97	OFF	1.5	1
43	99	OFF	1.5	1
44	101	OFF	1.5	1

b

Fig.6: Molecular composition detected by mass quadrupole in the deposition chamber prior to deposition(SIN49)

- a) Complete data in the molecular mass range 1-100.
- b) Partial pressure of 8 selected masses



a

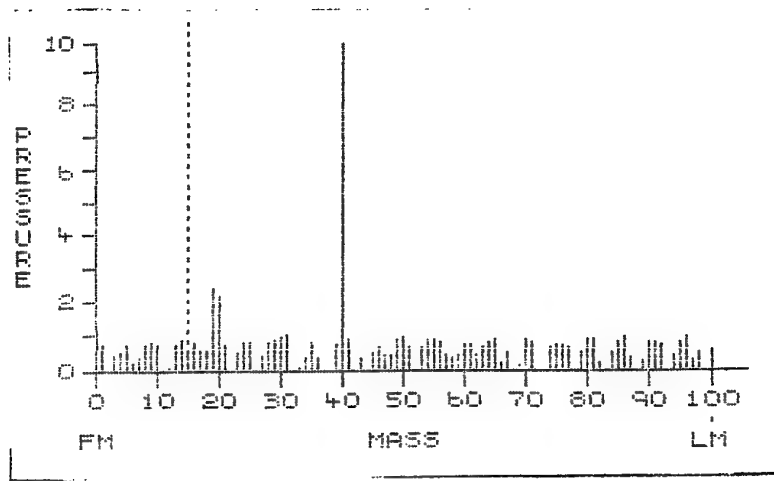
CHANNEL	MASS	ALARM	TORR	M/F
1	16	OFF	5.6 x 10 ⁻⁸ A	F
2	17	OFF	1.5 x 10 ⁻⁸ A	F
3	18	OFF	4.0 x 10 ⁻⁸ A	F
4	20	OFF	7.5 x 10 ⁻⁸ A	F
5	29	OFF	1.4 x 10 ⁻⁷ A	F
6	40	OFF	8.0 x 10 ⁻⁸ A	F
7	91	OFF	1.0 x 10 ⁻⁸ A	F
8	95	OFF	1.0 x 10 ⁻⁸ A	F
9	40	OFF	1.0 x 10 ⁻⁸ A	F
10	16	OFF	1.0 x 10 ⁻⁸ A	F
11	17	OFF	1.0 x 10 ⁻⁸ A	F
12	18	OFF	1.0 x 10 ⁻⁸ A	F
13	20	OFF	1.0 x 10 ⁻⁸ A	F
14	29	OFF	1.0 x 10 ⁻⁸ A	F
15	40	OFF	1.0 x 10 ⁻⁸ A	F
16	95	OFF	1.0 x 10 ⁻⁸ A	F

b

Fig.7: Molecular composition detected by mass quadrupole in the deposition chamber during continuous flow of $\text{NH}_3/\text{SiH}_4/\text{Ar}$ prior to laser operation in experiment SIN49

a) Complete data in the molecular mass range 1-100.

b) Partial pressure of 8 selected masses



a

CHANNEL	MASS	ALARM	TORR	M/F
1	15	OFF	1.1	T
2	16	OFF	1.1	T
3	17	OFF	1.1	T
4	18	OFF	1.1	T
5	19	OFF	1.1	T
6	20	OFF	1.1	T
7	21	OFF	1.1	T
8	22	OFF	1.1	T
9	23	OFF	1.1	T
10	24	OFF	1.1	T
11	25	OFF	1.1	T
12	26	OFF	1.1	T
13	27	OFF	1.1	T
14	28	OFF	1.1	T
15	29	OFF	1.1	T
16	30	OFF	1.1	T
17	31	OFF	1.1	T
18	32	OFF	1.1	T
19	33	OFF	1.1	T
20	34	OFF	1.1	T
21	35	OFF	1.1	T
22	36	OFF	1.1	T
23	37	OFF	1.1	T
24	38	OFF	1.1	T
25	39	OFF	1.1	T
26	40	OFF	1.1	T
27	41	OFF	1.1	T
28	42	OFF	1.1	T
29	43	OFF	1.1	T
30	44	OFF	1.1	T
31	45	OFF	1.1	T
32	46	OFF	1.1	T
33	47	OFF	1.1	T
34	48	OFF	1.1	T
35	49	OFF	1.1	T
36	50	OFF	1.1	T
37	51	OFF	1.1	T
38	52	OFF	1.1	T
39	53	OFF	1.1	T
40	54	OFF	1.1	T
41	55	OFF	1.1	T
42	56	OFF	1.1	T
43	57	OFF	1.1	T
44	58	OFF	1.1	T
45	59	OFF	1.1	T
46	60	OFF	1.1	T
47	61	OFF	1.1	T
48	62	OFF	1.1	T
49	63	OFF	1.1	T
50	64	OFF	1.1	T
51	65	OFF	1.1	T
52	66	OFF	1.1	T
53	67	OFF	1.1	T
54	68	OFF	1.1	T
55	69	OFF	1.1	T
56	70	OFF	1.1	T
57	71	OFF	1.1	T
58	72	OFF	1.1	T
59	73	OFF	1.1	T
60	74	OFF	1.1	T
61	75	OFF	1.1	T
62	76	OFF	1.1	T
63	77	OFF	1.1	T
64	78	OFF	1.1	T
65	79	OFF	1.1	T
66	80	OFF	1.1	T
67	81	OFF	1.1	T
68	82	OFF	1.1	T
69	83	OFF	1.1	T
70	84	OFF	1.1	T
71	85	OFF	1.1	T
72	86	OFF	1.1	T
73	87	OFF	1.1	T
74	88	OFF	1.1	T
75	89	OFF	1.1	T
76	90	OFF	1.1	T
77	91	OFF	1.1	T
78	92	OFF	1.1	T
79	93	OFF	1.1	T
80	94	OFF	1.1	T
81	95	OFF	1.1	T
82	96	OFF	1.1	T
83	97	OFF	1.1	T
84	98	OFF	1.1	T
85	99	OFF	1.1	T
86	100	OFF	1.1	T

b

Fig.8: Molecular composition detected by mass quadrupole in the deposition chamber during continuous flow of $\text{NH}_3/\text{SiH}_4/\text{Ar}$ and laser irradiation in experiment SIN49

- a) Complete data in the molecular mass range 1-100.
- b) Partial pressure of 8 selected masses

Figs. 9-10 show the dependence of the concentration ratio of NH_2/NH_3 on the number of pulses. These type of plots can indicate on the photochemical reaction channel during laser irradiation. The curve in fig.9 show that up to 20000 pulses the NH_2/NH_3 ratio was almost constant and it's value was about 0.15, followed by a linear dependence up to a ratio of 0.7 which was obtained at the end of the experiment, after 40000 pulses (SIN42). This behavior was found also in experiment SIN47 (Fig.10) and SIN49 (Fig.11) which were carried out at the same SiH_4/NH_3 ratio although the absolute flow rate was changed. From these results it can be concluded that the deposition rate is not constant during deposition and it's value is very low at the beginning of the experiment and it increases after about 20000 pulses. Looking at the thickness measurements in table 2 one can see indeed that the thickness after 100000 pulses is higher than expected from linear calculation which is based upon the thickness of the films which were obtained at 40000 pulses.

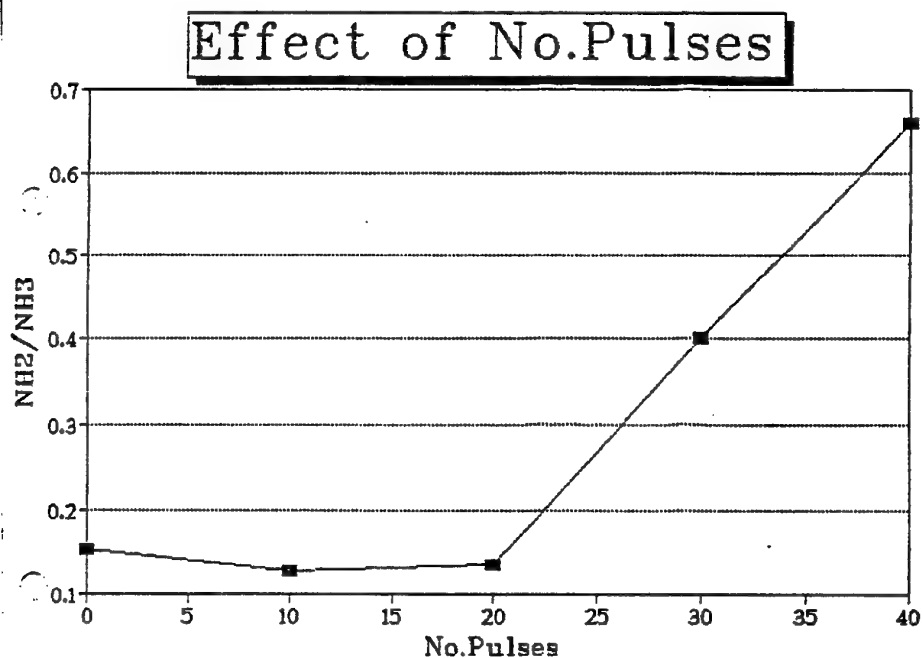


Fig.9: NH_2/NH_3 dependence on the number of pulses in experiment SIN42

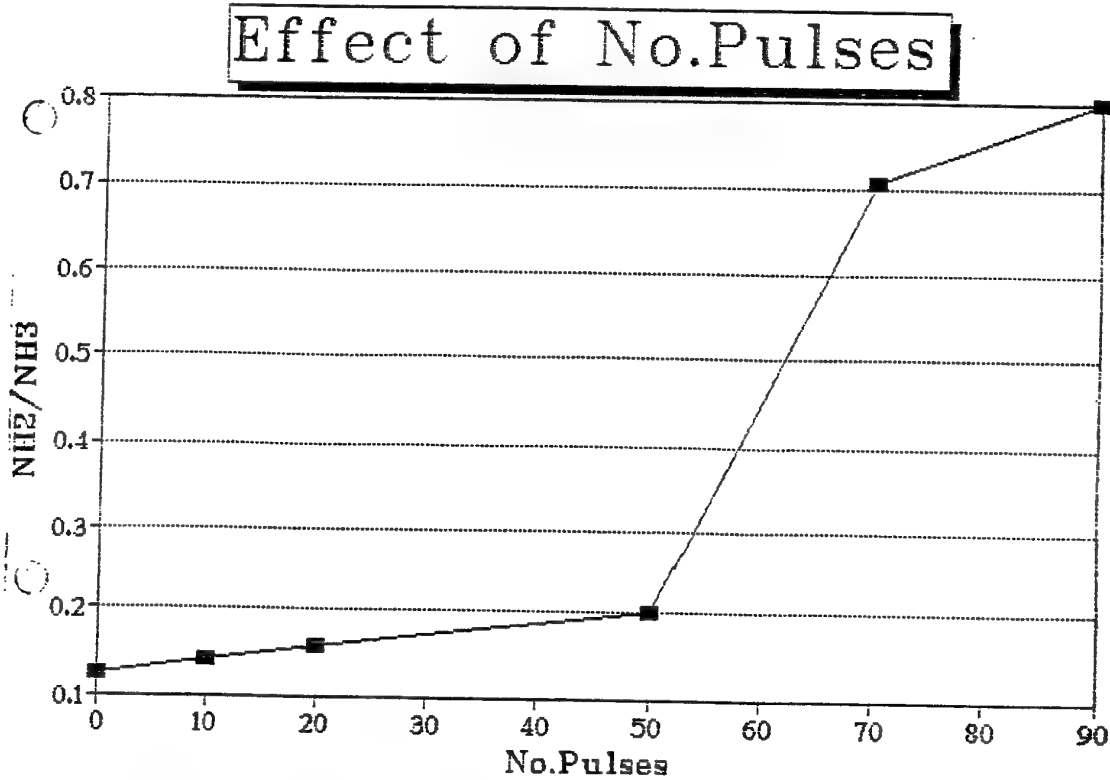


Fig.10: NH_2/NH_3 dependence on the number of pulses in experiment SIN47

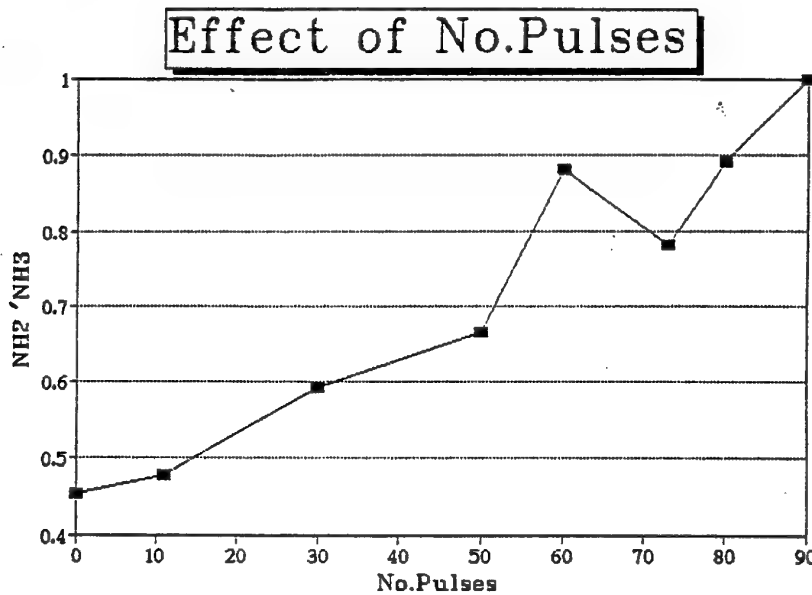


Fig.11: NH_2/NH_3 dependence on the number of pulses in experiment SIN49

4. SUMMARY

In this year we studied the deposition of silicon nitride thin films at low temperatures. Amorphous silicon nitride films with good adhesion and optical properties were obtained at a minimum temperature of 120°C.

The Si/N ratio in these films ranges between 0.5-0.9 but no correlation could be made between the film composition and substrate temperature. The refractive index of the various films was 1.75-2.2. A value of refractive index below 2.0 is attributed to the presence of hydrogen in the silicon nitride film. The hydrogen composition couldn't be measured quantitatively however, it can be assumed that its amount is increased at low temperature.

In this year we also managed to settle a new line for acetylene gas and to do some preliminary experiments for silicon carbide deposition. This process is only in the beginning and it still has to be optimized.

Appendix A

LASER INDUCED CHEMICAL VAPOR DEPOSITION
OF THIN FILMS

PROGRESS REPORT NO.1 (1-3/94)

CONTRACT NO. F61708-94-C0002

LASER INDUCED CHEMICAL VAPOR DEPOSITION OF THIN FILMS

PROGRESS REPORT NO.1 (1-3/94)

CONTRACT NO. F61708-94-C0002

Submitted by

**Dr. S. Tamir & Dr. J. Zahavi
Israel Institute of Metals, Technion,
Haifa, Israel**

Haifa, March 31, 1994

INTRODUCTION

The aim of this project is to develop and to investigate a deposition process for the formation of thin films using laser irradiation. The idea is to use excimer laser beam at a wavelength of 193 nm, for the dissociation of gas molecules and to obtain in this way deposition of films at low temperature, with a sharp interface between the film and the substrate and also to get films with low internal stresses. The work in this year will concentrate upon deposition of silicon nitride and silicon carbide films.

The first stage was to modify our experimental system which was used for deposition of silicon and silicon nitride by the addition of gas feeding line for acetylene which will be the source of carbon for silicon carbide deposition. In addition, the optical system was also modified in order to get an homogenous intensity distribution in the beam cross section which must be use in a case that the irradiation is carried out in perpendicular to the substrate.

EXPERIMENTAL

Deposition System

A picture of the experimental system is shown in Fig.1. It consists of a stainless steel chamber connected to a turbomolecular pump which is backed by a mechanical pump. Prior to the deposition the chamber is evacuated to a base vacuum of about 10^{-6} Torr, and the specimen is heated. The process gas or gas mixture flows through several lines and mass flow controllers and are mixed before entering the chamber. The picture shown in Fig.2 exhibits the mass flow controllers for ammonia, silane, acetylene and argon. The line for Ar was also changed in order to control the amount of this gas that is used for washing the window where the

laser beam enters the chamber. Ar gas flow is important in

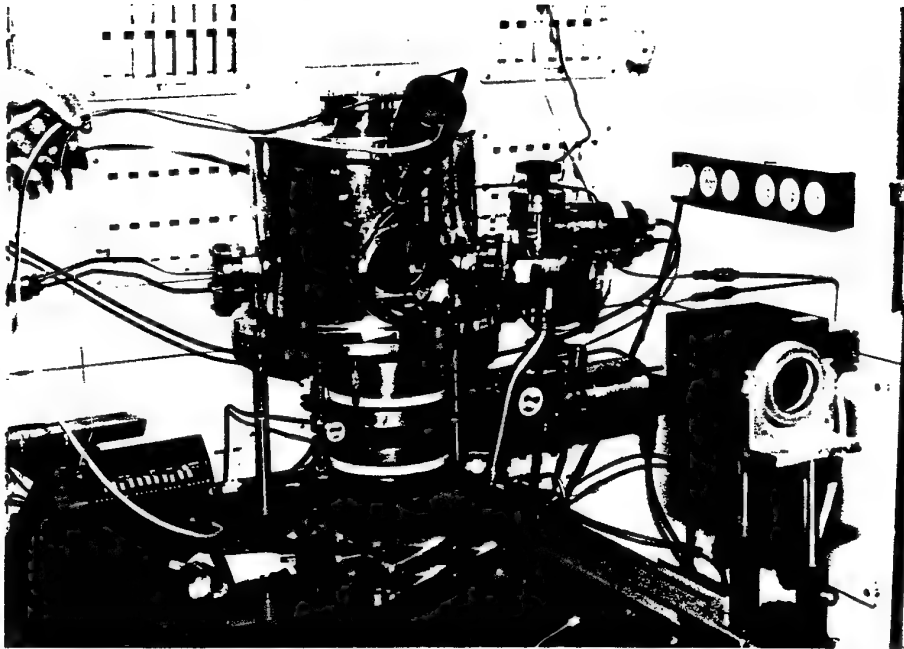


Fig. 1: The experimental system for laser induced chemical vapor deposition.



Fig. 2: General view of the gas feeding lines.

order to prevent deposition on the window. When the whole system reach steady state of at a constant gas flow rate and substrate temperature the laser beam is allowed to enter the chamber and the deposition starts. During deposition the beam is directed into a quartz tube travelling in parallel to the substrate.

MATERIALS

Substrate

Silicon nitride and silicon carbide films will be deposited on Si(100) single crystal. The specimens 40mm*10mm are cut from a 8" wafers which are used in the fabrication of integrated circuits.

Gases

The investigation of silicon nitride deposition will be carried out in a gas mixture of silane and ammonia. The ammonia has absorption cross section in the order of 10^{-16} cm² which is well enough to promote a photochemical dissociation of the molecule which is needed for the chemical reaction with silane to produce silicon nitride. The ammonia gas is also generally used in thermal and plasma assisted CVD.

The choice of gas source for carbon which is needed for the deposition of silicon carbide was more difficult. In general, molecule with carbon-carbon bond intend to absorb the photon of the excimer laser and to dissociate. Acetylene gas was preferred due to the fact that this molecule has a triple bond and the molecule is more active than the saturated hydrocarbons.

All gasses used have a purity of electronic grade.

Optical System

The optical system consists of beam homogenizer, lens, attenuator, and camera. The beam coming out from the laser has a rectangular cross section with dimension of $20 \times 5 \text{ mm}^2$ with a hollow circle inside it. The intensity distribution is not homogenous, as is expected from a multimode laser beam, with energy distribution as shown in Fig.3. Fig.3a shows three dimensional energy distribution and Fig.3b shows the relative intensity along the horizontal line in the middle of the beam cross section. These graphs are obtained from the computer which gets the intensity signal from the camera. The camera is also connected to a screen on which the laser beam can be viewed and the intensity distribution is observed by different colors representing different intensities. the attenuator is located before the camera in order to protect it, and they both are removed from the beam path when deposition starts. After the beam passes through the homogenizer and the focusing lens, the beam has rectangular cross section of $4 \times 4 \text{ mm}^2$ at the focal point and its energy distribution is shown in Fig.4.

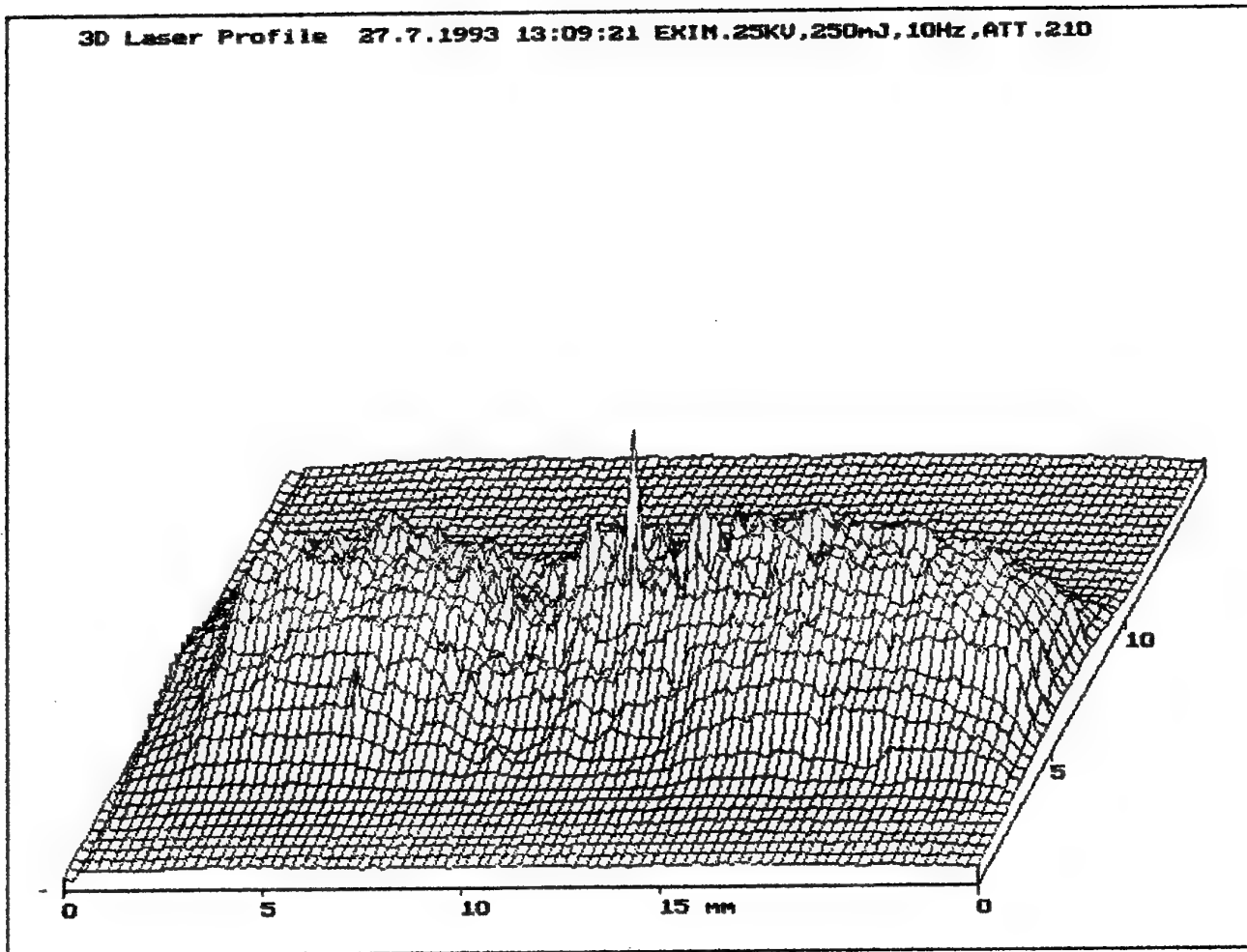


Fig 3: Three dimensional intensity distribution of laser beam (a) and intensity profile along the beam center (b) before homogenizer

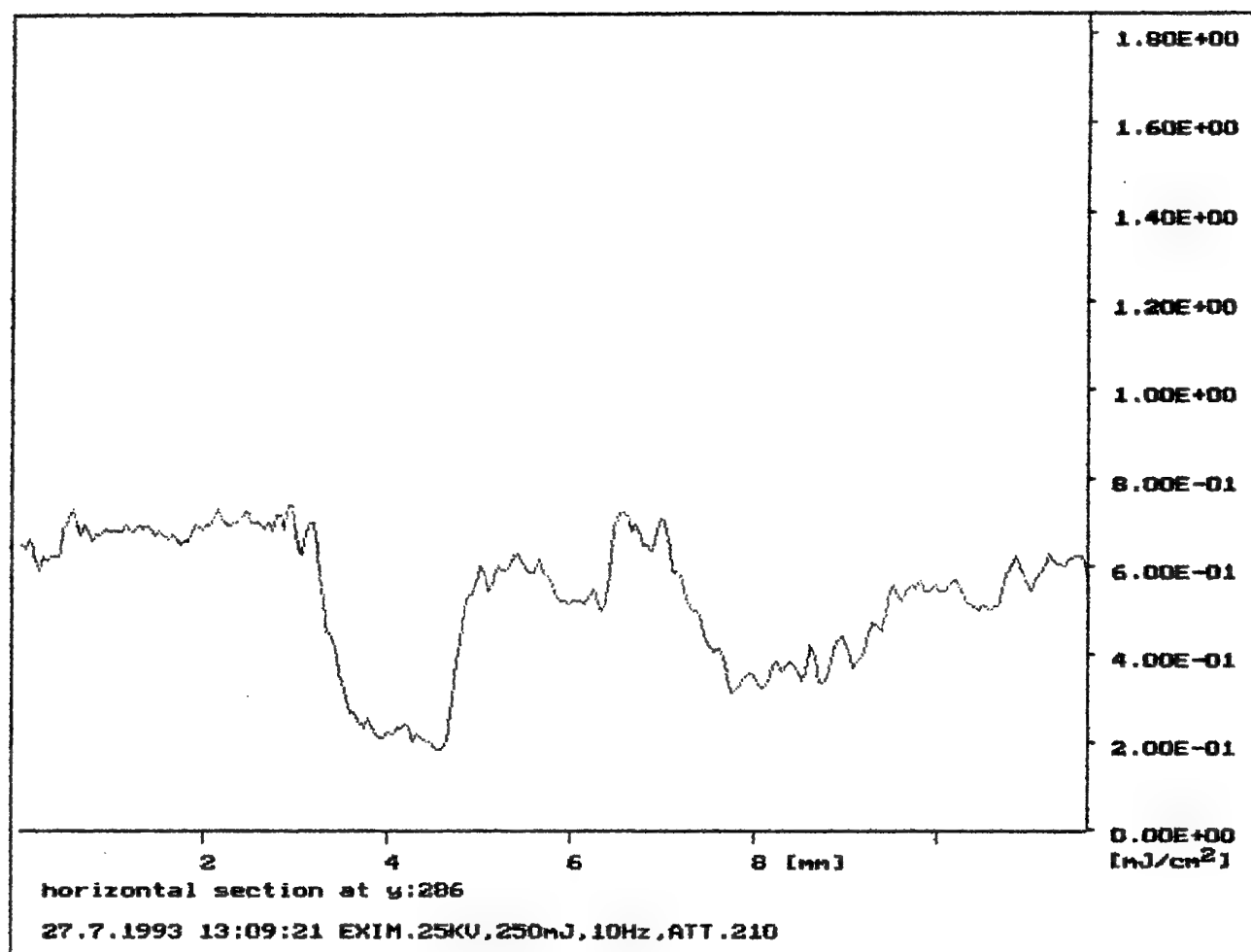


Fig. 3: (Cont.)

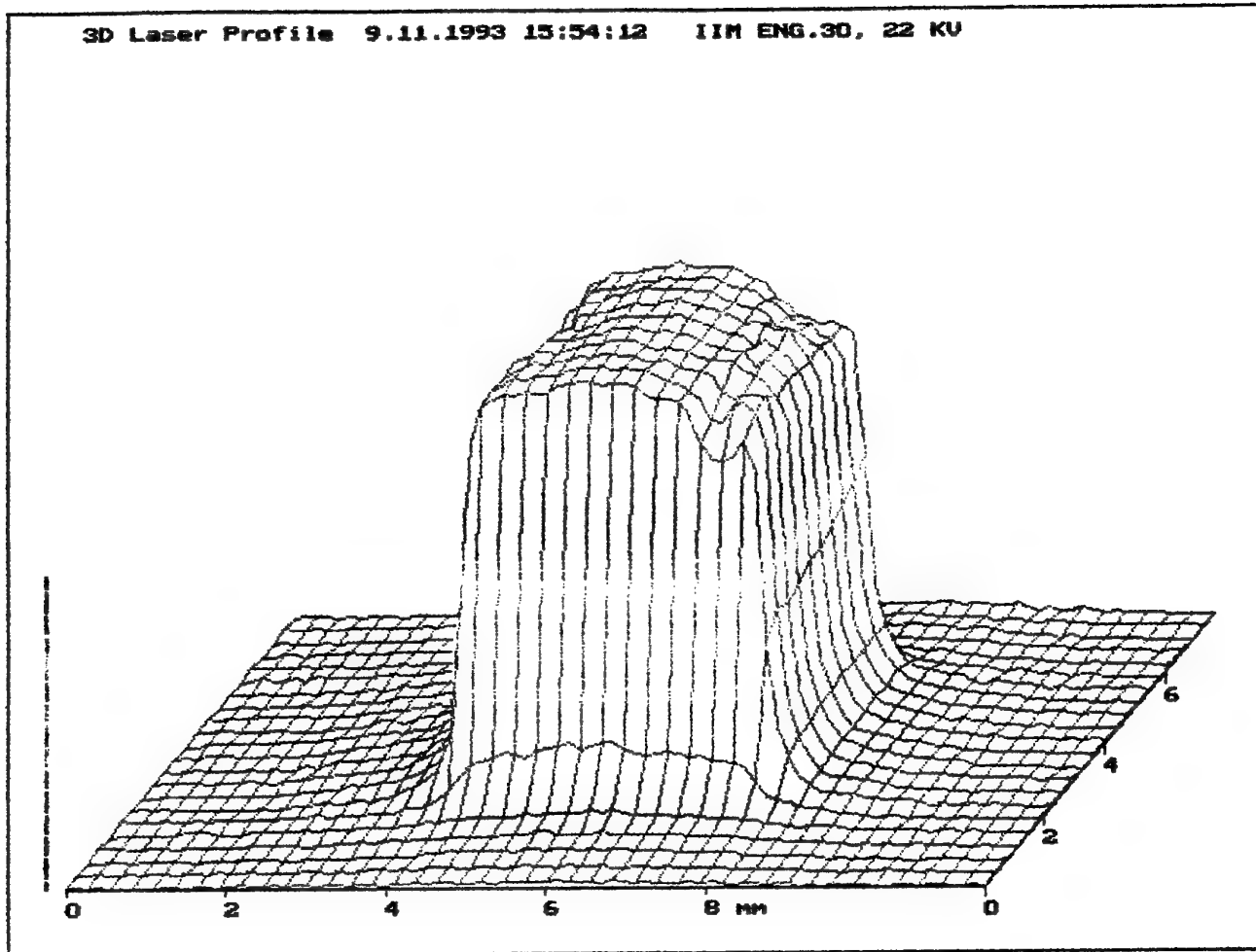


Fig 4: Three dimensional intensity distribution of laser beam (a) and intensity profile along the beam center (b) before homogenizer

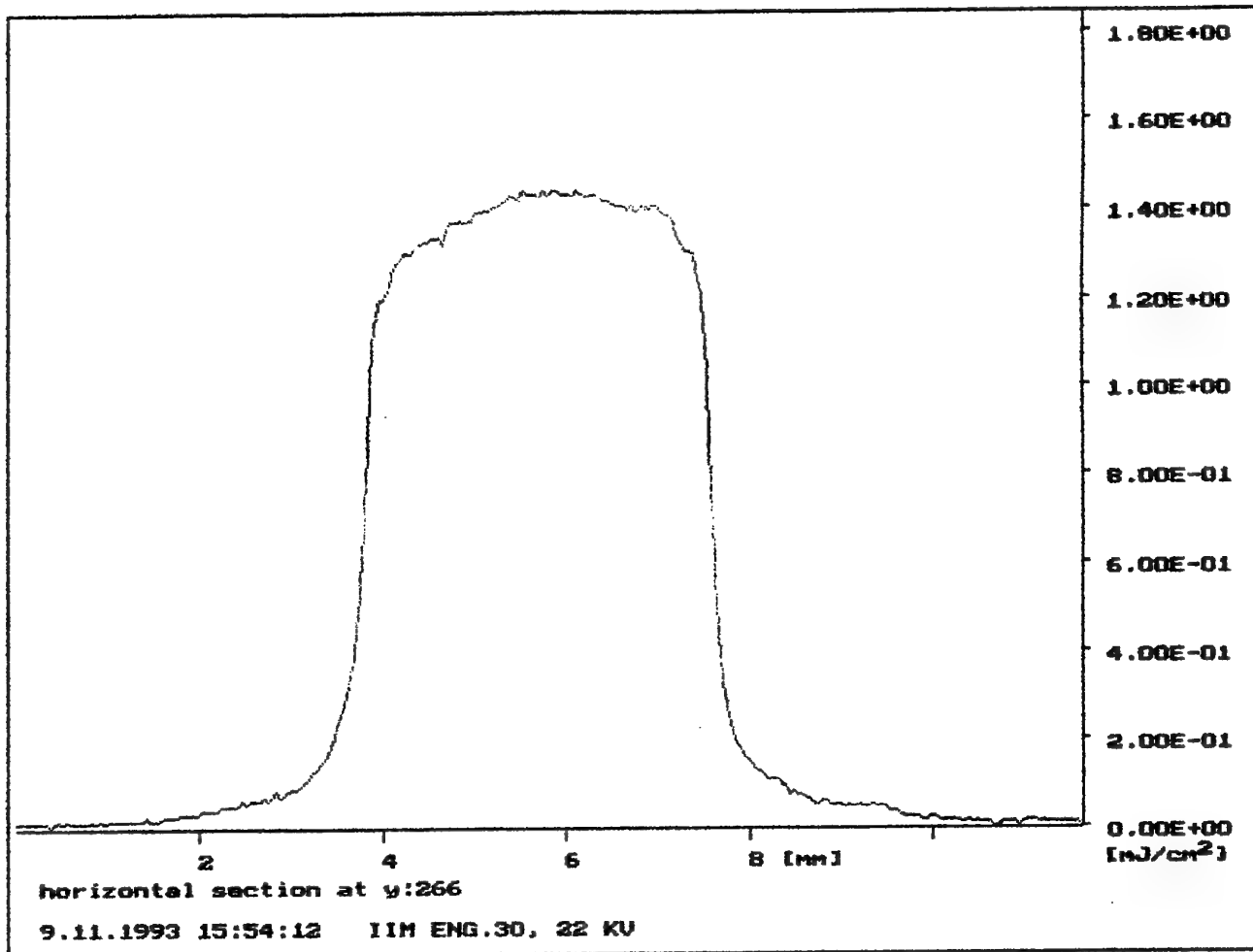


Fig. 4: (Cont.).

EXPERIMENTS

The designing of the experiments is based upon the results obtained so far in this system. The work done up to now was concentrated upon studying the process of deposition of silicon and silicon nitride. Silicon nitride films were obtained at a temperature 400-650°C, a constant gas flow rate, constant temperature and constant SiH_4/NH_3 ratio. Fig.5 shows a general view of a silicon nitride film deposited on Si(100). The film was obtained by irradiating the gas mixture while the beam was travelling in parallel to the substrate. The blue and yellow color represents differences of film thickness. The thickness distribution can be avoided by scanning of the laser beam, however this can't't be tested yet in the experimental system and further modification of the deposition system is needed. The measured refractive index of the film shown in Fig.5 is 2.04 which indicates that a stoichiometric composition of Si_3N_4 was formed. The compositional profile of the film as analyzed by Auger Electron Spectroscopy is shown in fig 6. The curves in the figure show that a constant Si/N ratio of about 0.75 is measured along the whole thickness of the film.

In the following experiments the effect of decreasing temperature, and the change in SiH_4/NH_3 ratio on the composition and structure of the films will be studied, and the refractive index will be measured.

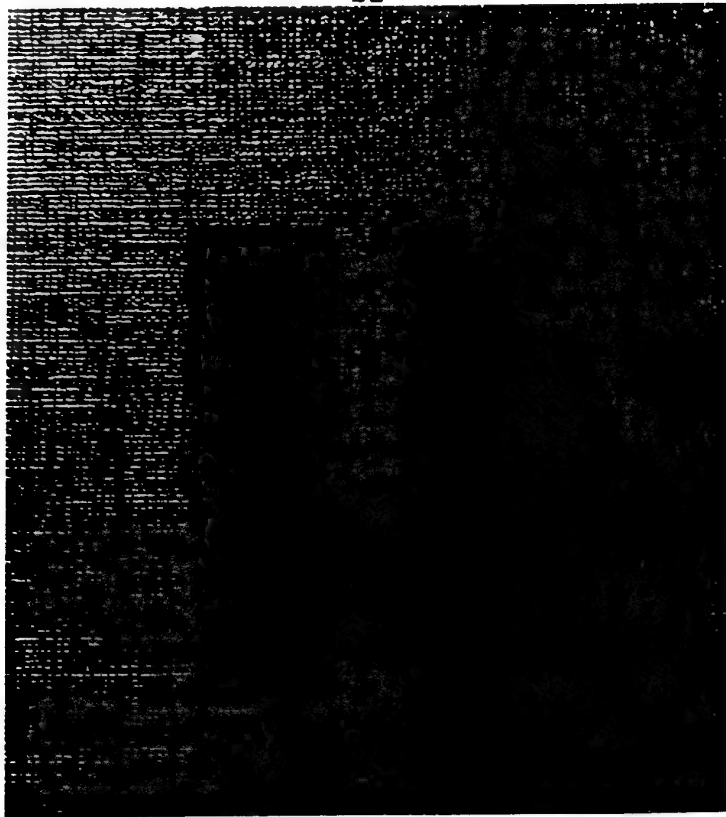


Fig 5: General view of silicon nitride film prepared by LCVD

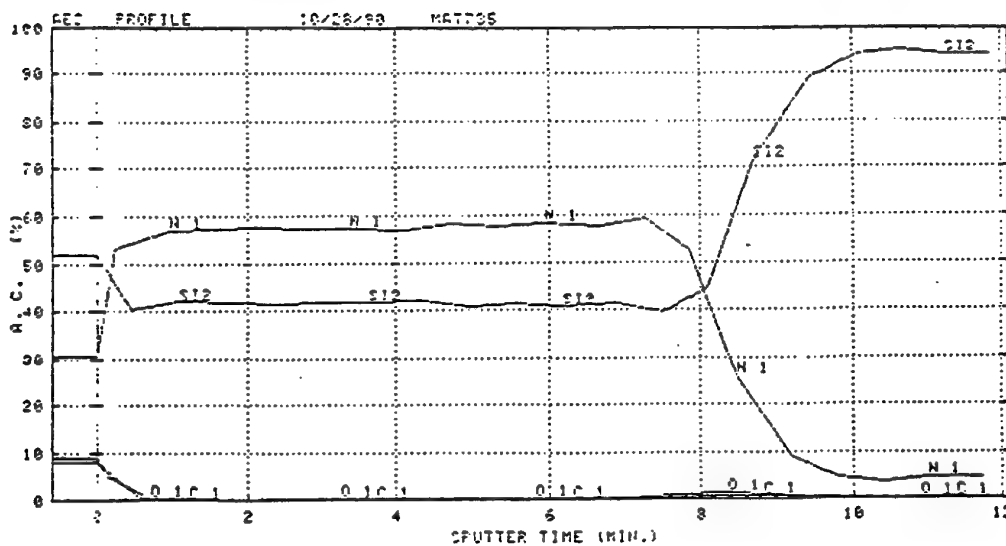


Fig.6: Elements concentration profile of silicon nitride prepared by LCVD analyzed by Auger Electron Spectroscopy.

Appendix B

LASER INDUCED CHEMICAL VAPOR DEPOSITION
OF THIN FILMS

PROGRESS REPORT NO.2

CONTRACT NO. F61708-94-C0002

LASER INDUCED CHEMICAL VAPOR DEPOSITION OF THIN FILMS

PROGRESS REPORT NO.2 (4-8/94)

CONTRACT NO. F61708-94-C0002

Submitted by

Dr. S. Tamir & Dr. J. Zahavi
Israel Institute of Metals, Technion,
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Haifa, September 1994

INTRODUCTION

According to the second stage of the research program the aims of the experiments were to study the effect of deposition temperature below 400°C on film quality, microstructure and composition of silicon nitride. The experiments showed that it is possible to obtain smooth and shiny films at temperature as low as 250°C. Ellipsometric measurements showed that the refractive indices of the films ranged between 2.0-2.5 at temperature range of 250-400°C, depending upon film thickness. the Si/N ratio was changed by changing deposition temperature, in contrast to earlier results which were obtained at temperature range of 400-650°C.

EXPERIMENTS

Table 1 lists the deposition conditions of the experiments for the formation of silicon nitride at low temperature range.

The gas mixture consists of ammonia/silane(15%Ar) at flow rate of 7.5 SCCM/25 SCCM, respectively. In addition a constant flow of 100 SCCM Ar was supplied to the chamber window at the irradiated area in order to prevent deposition on it while the beam is travelling into the deposition chamber and therefore, to maintain minimum absorption of the laser beam by the window.

The value of the pressure which appears in the table is the total pressure at the chamber including the washing Ar gas. When a total pressure of 6.6 Torr was measured the partial pressure of the ammonia/silane mixture was 3.5 Torr. Basically, the main parameter which was changed was substrate temperature, however, other parameters were also changed according to the results of each experiment in order to eliminate the formation of unwanted powdered films.

Table No.1: List of experiments and experimental parameters
for deposition of silicon nitride films

Exp#	Temperature °C	Pressure Torr	Repetition Rate (Hz)	Laser Energy mJ	No. Pulses
SIN30	400	5.9	20	190	50000
SIN31	300	6.4	20	210	50000
SIN32	200	6.5	20	210	50000
SIN33	250	5.8	20	150	32000
SIN34	250	6.5	20	200	50010
SIN35	200	6.3	20	170-130	50003
SIN36	200	6.1	5	170	30012

RESULTS AND DISCUSSION

Films quality

Macro pictures of the various films are presented in Fig.1. The films which are classified as good films are those which were formed in runs SIN30, SIN31, SIN34. These films had good spectral reflectance and therefore could be easily

analyzed by using ellipsometry. These films had also good adhesion to the substrate. The films obtained from runs SIN32, SIN33, SIN35 and SIN36 were not satisfactory and had a powdered form which could be removed easily from the substrate. The different colors which appears on the surface of the good films are known to be due to thickness differences as will be further explained in the discussion thickness measurements results.



Fig. 1: Macro view of SIN films obtained by LCVD from ammonia/silane gas mixture.

Films Composition

The composition of elements of SIN films as was analyzed by AES is shown in Fig. 3-7. The analyses in the as received samples of all films show that the films contains also carbon and oxygen which results from exposure of the

specimens to impurities in the atmosphere. This result is similar also in the reference film which was obtained at low pressure CVD (LPCVD - fig2).

Also shown in each figure a compositional profile along film thickness. At temperature of 400°C (SIN30 - Fig.3) the films has a constant ratio of $Si/N = 1$ which is different from $Si/N=0.75$ which was found for Si_3N_4 which was obtained in earlier study and also at the reference sample. The oxygen concentration in the film is low and is identified to the concentration in the reference sample. A rough estimation of film thickness using the compositional profile can be obtained by multiplying the sputtering rate by sputtering time. The calculated thickness at the measuring point is 180 nm. At a temperature of 300°C (SIN31-Fig.4) The compositional profile shows that the $Si/N = 0.55$. This ratio is constant along film thickness, however it is different from the composition of the film which was obtained at 400°C. It can also be observed that the film contains almost 10% of oxygen which is not allowed in the film. The peak in oxygen concentration near the interface between the film and the substrate is related to a bad cleaning treatment of the surface prior to deposition. The estimated film thickness at the measurement point is 75 nm. Figs 5-6 show the AES results of films which were obtained at a temperature of 250°C. The comparison between these two different results is very important. These two experiments had been conducted at the same deposition conditions and therefore we would expect similar composition of the films. However the film which was obtained at run SIN33 was powdered and the film produced at run SIN34 had good quality and good spectral reflectance. Indeed, the compositional profile of the good film showed almost constant ration of $Si/N = 0.8$ and oxygen concentration below 10%. It should be emphasized that the oxygen concentration is far beyond the permitted value which is below 1%.

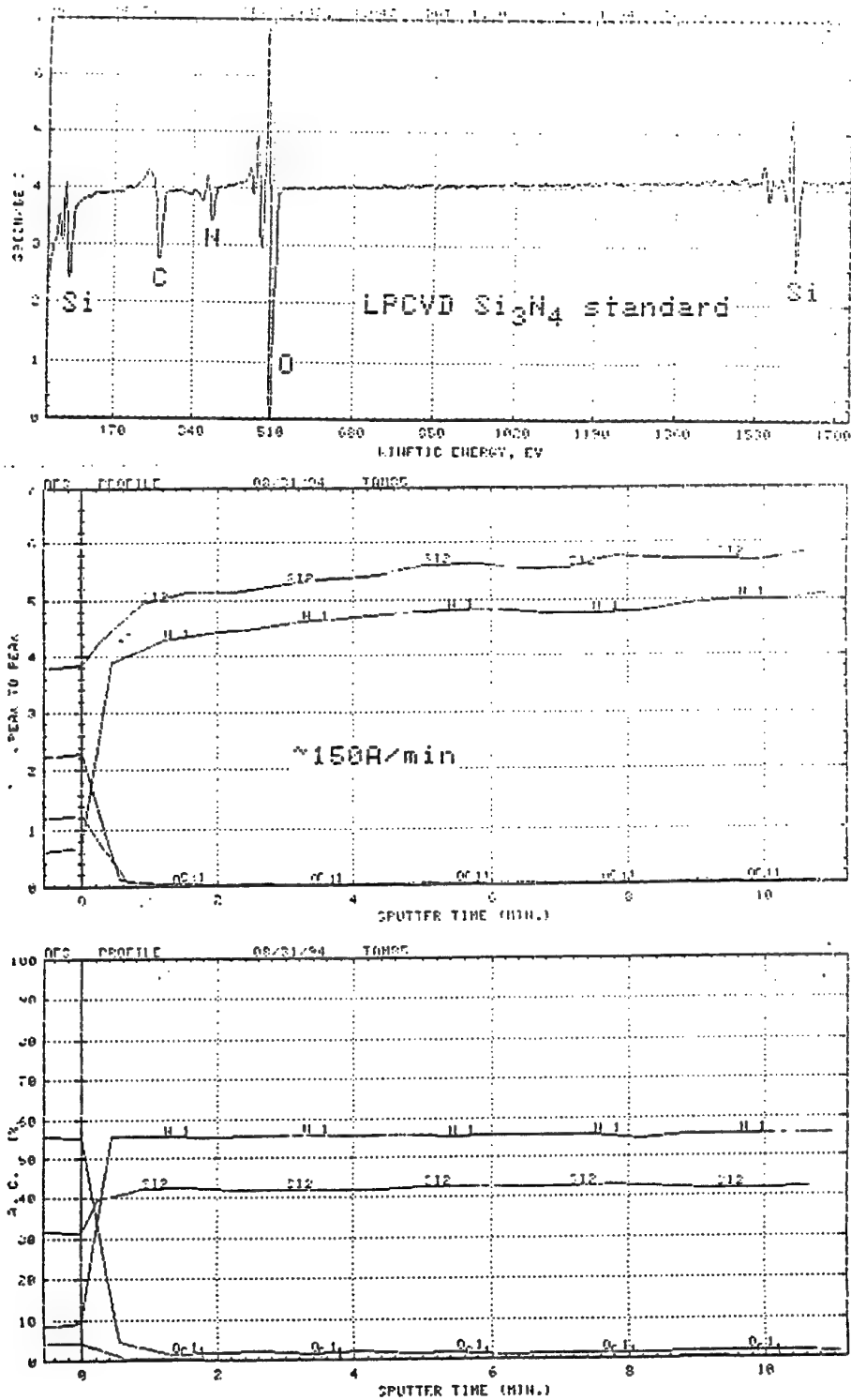


Fig.2: As deposited surface composition (a) and compositional profile (b: peak to peak and c: atomic concentration) of silicon nitride reference film deposited at Low Pressure CVD

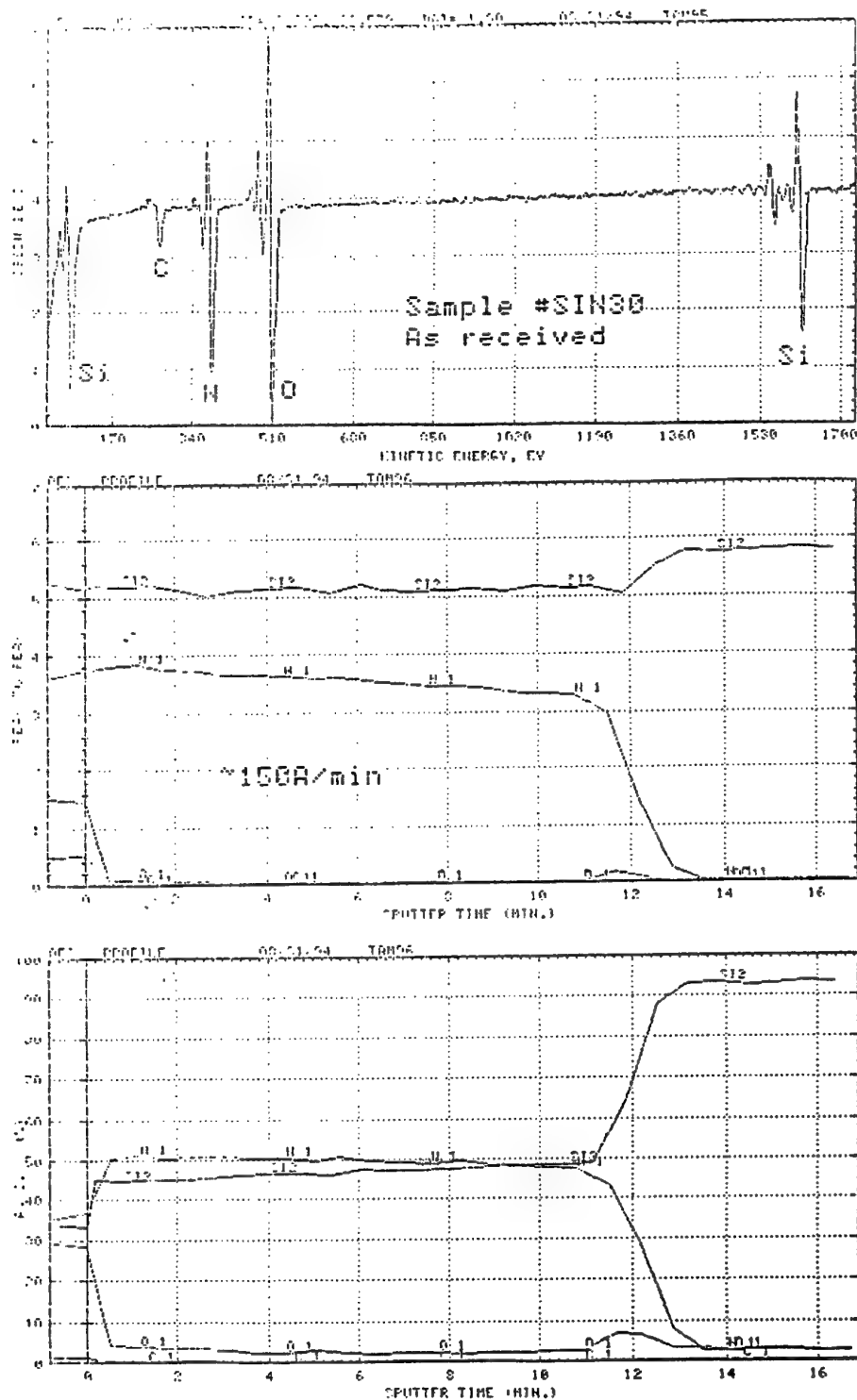


Fig.3: As deposited surface composition (a) and compositional profile (b: peak to peak and c: atomic concentration) of silicon nitride film deposited at 400°C (run SIN30).

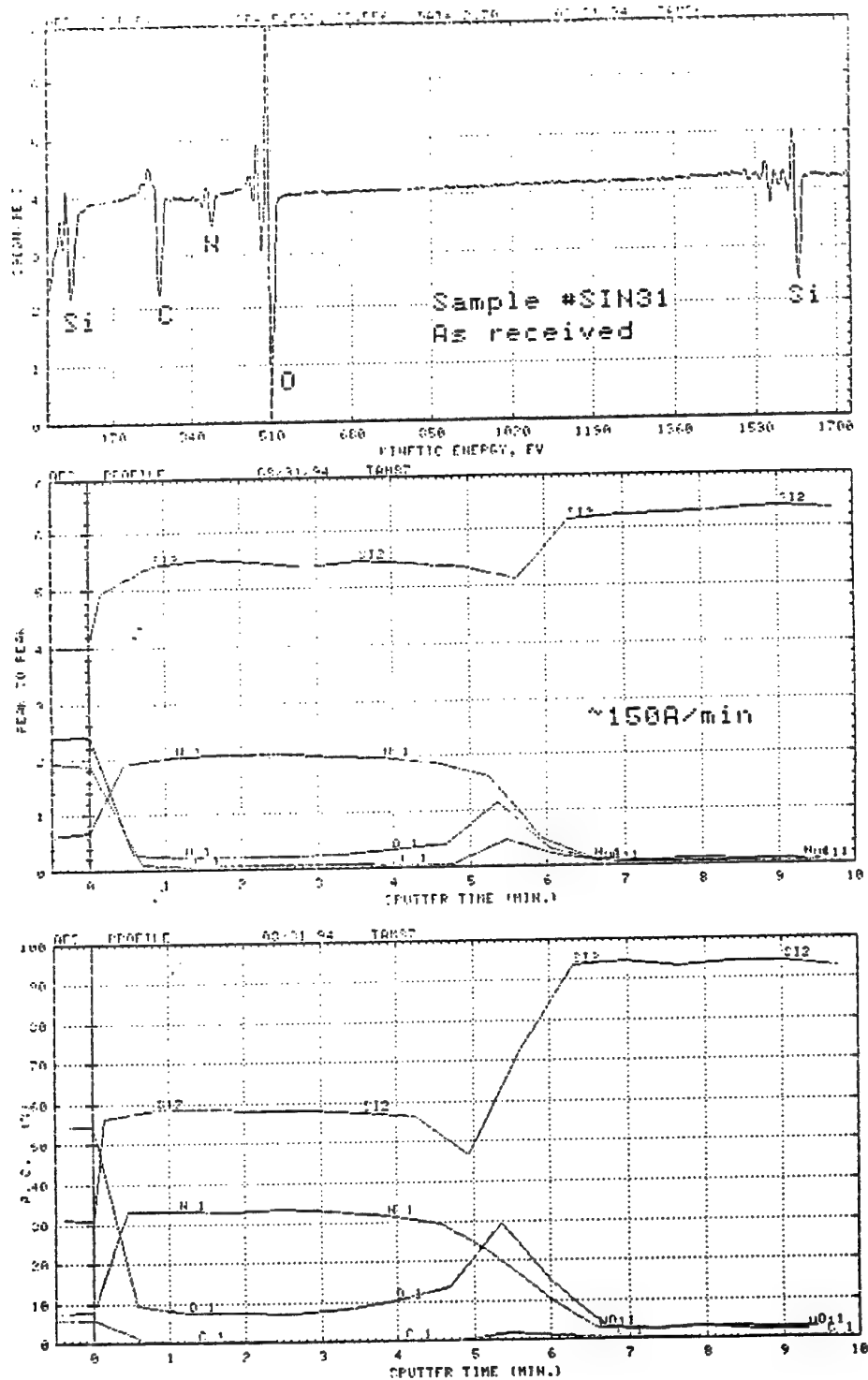


Fig.4: As deposited surface composition (a) and compositional profile (b:peak to peak and c: atomic concentration) of silicon nitride film deposited at 300°C (run SIN31).

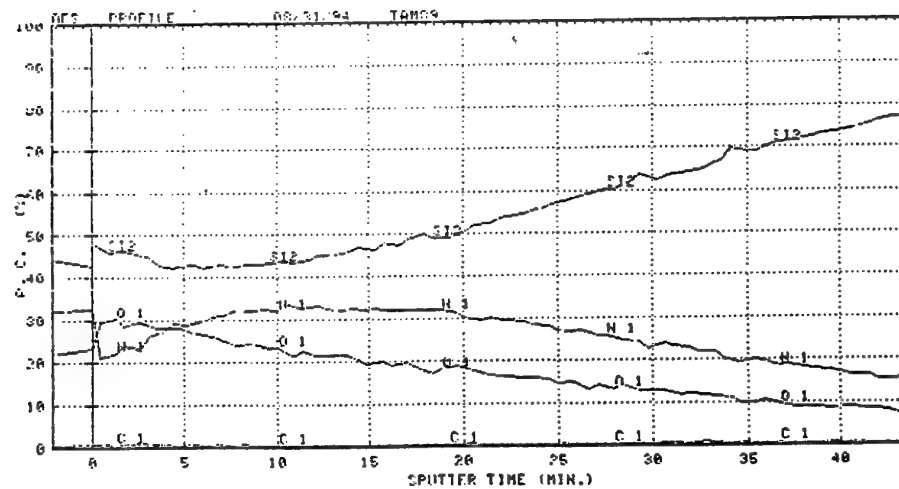
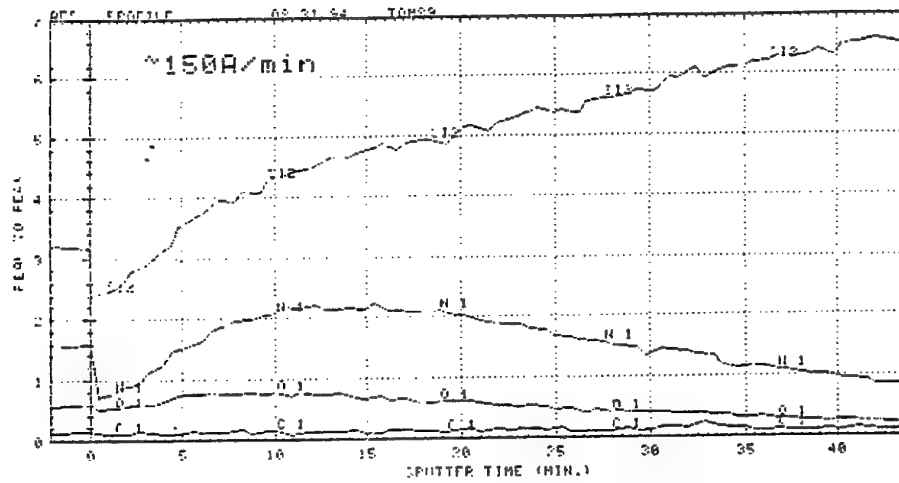
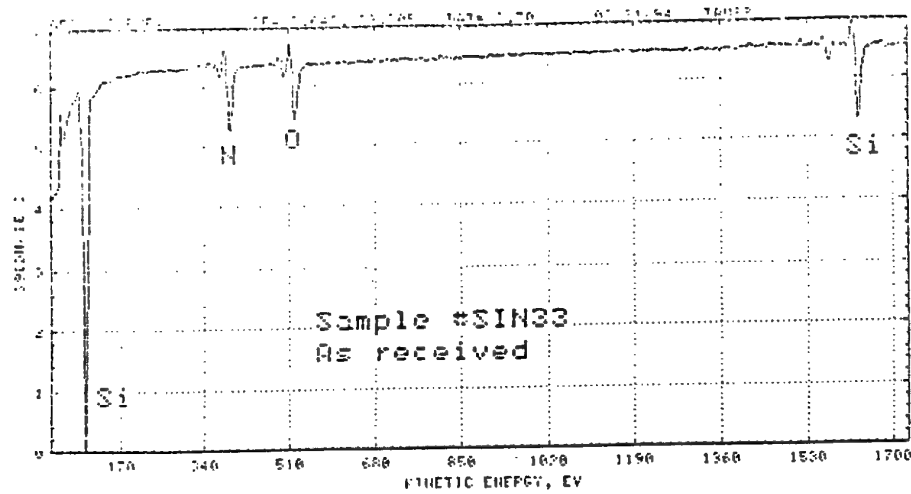


Fig.5: As deposited surface composition (a) and compositional profile (b: peak to peak and c: atomic concentration) of silicon nitride film deposited at 250°C (run SIN33).

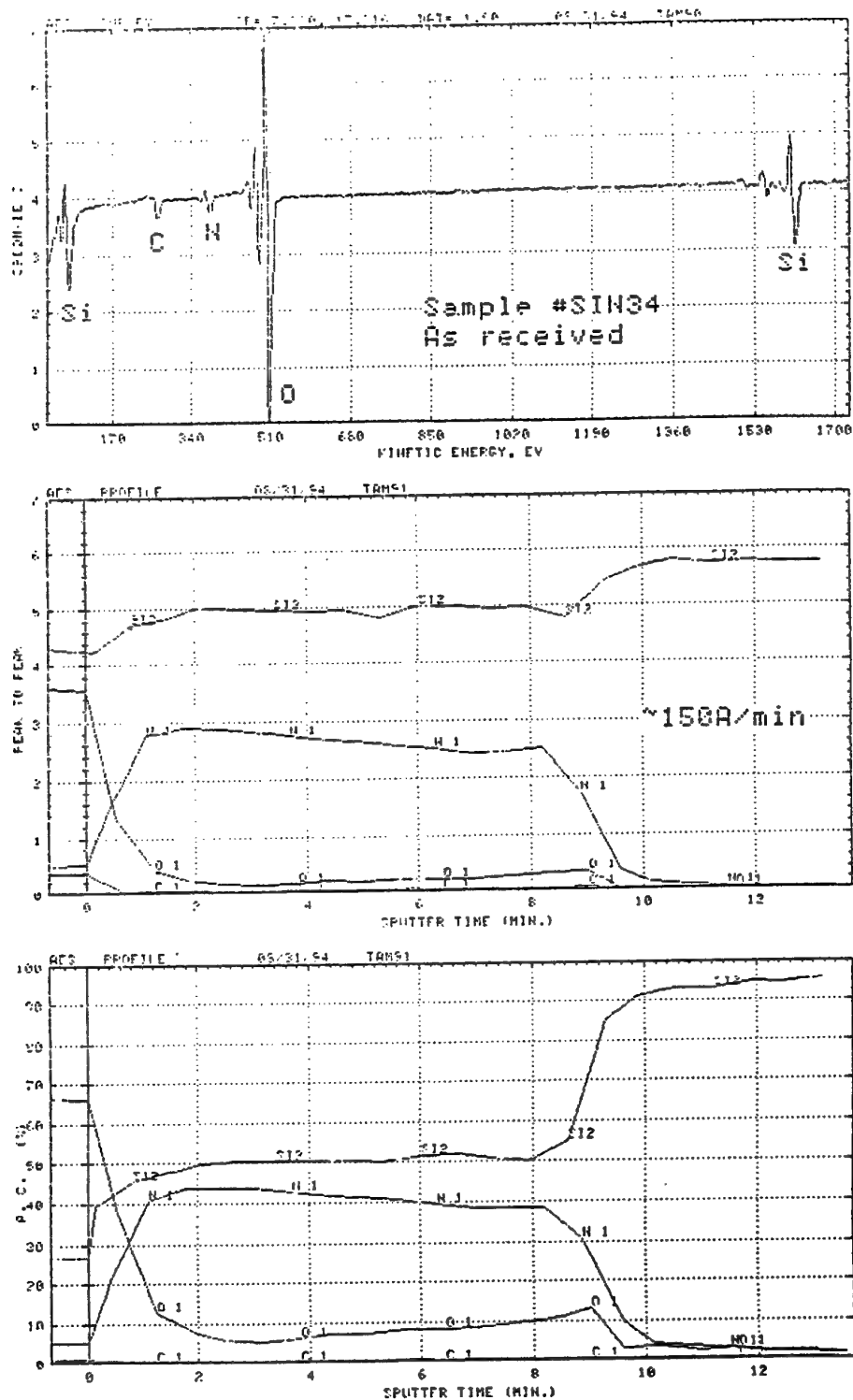


Fig.6: As deposited surface composition (a) and compositional profile (b: peak to peak and c: atomic concentration) of silicon nitride film deposited at 250°C (run SIN34).

The compositional profile of the powdered film showed that the amount of silicon and nitrogen is not constant along the film thickness, the oxygen concentration is too high (20-34%) and there is no sharp interface as is usually expected from good quality films. So far we can't find a reasonable explanation for this result except that one of the deposition parameter was not under control, for example the gas flow rate. The conclusion is verified by the high amount of oxygen in the deposition chamber and also in the film which was never detected in earlier experiments in this system. It is important to mention that when a powdered film is formed an illumination is viewed during laser irradiation in the gas phase at the beam propagation path. This phenomenon was known before in silicon deposition and therefore it may be concluded that more experiments have to be done in order to investigate the reasons for this phenomenon and to prevent it in order to get non powdered film. The compositional profile of the film obtained at 200°C showed that at this experiment a rather unexpected result was obtained. Actually, instead of the formation of silicon nitride was formed but rather a SiO_2 film was formed. The source for the oxygen is not known, and verify the conclusion made from experiment SIN33 that factors other than substrate temperature was responsible for the bad results.

Thickness and Refractive Index Measurements

As was mentioned in the discussion of the macro pictures the silicon nitride films exhibited several colors which is known from previous work result from differences in film thickness. The reasons for thickness differences are not understood especially due to the fact that the beam cross area is rectangular and no focusing of the beam is done. These differences can't be measured by alpha step profiler which was also used for film thickness measurements but by

using ellipsometer. Using ellipsometer it was possible to make thickness and refractive index measurements at the same time. These measurements were done at many points along the two axis of the specimens surface. Fig. 7 shows the transversal thickness distribution profile at a point which is 2 cm from the front edge of the specimen. It is clear that a symmetrical type of thickness distribution curve is obtained even though it is not completed from the two sides of the peak maximum. It can reasonably assumed that if the specimen width was larger than 10 mm the complete curve would be recorded. The maximum thickness is 140 nm and it is obtained at the point which has the lowest distance from the center of the laser beam. The thickness drops to 60 nm at a distance of 5 mm from the peak value.

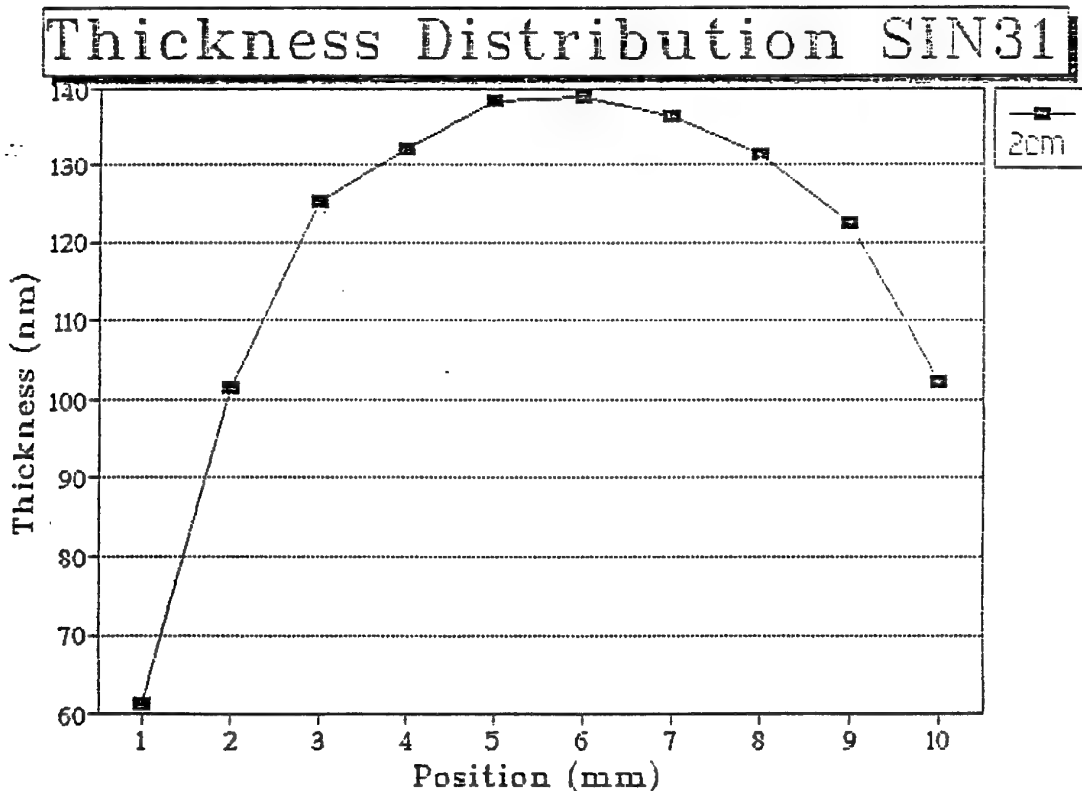


Fig 7: Transversal thickness distribution profile of silicon nitride films deposited at 300°C (run SIN31)

Thickness distribution profiles of the film deposited at 250°C (run SIN34) are shown in Fig.8. This figure shows the profile at four distances from the front edge of the specimen. The shape of the profiles and the maximum thickness are similar in each distance however, the peak width at 1 and 2cm are more wide than the peak width at 3 and 4 cm from the front edge. These results should be further investigated in order to study the mechanism of film growth.

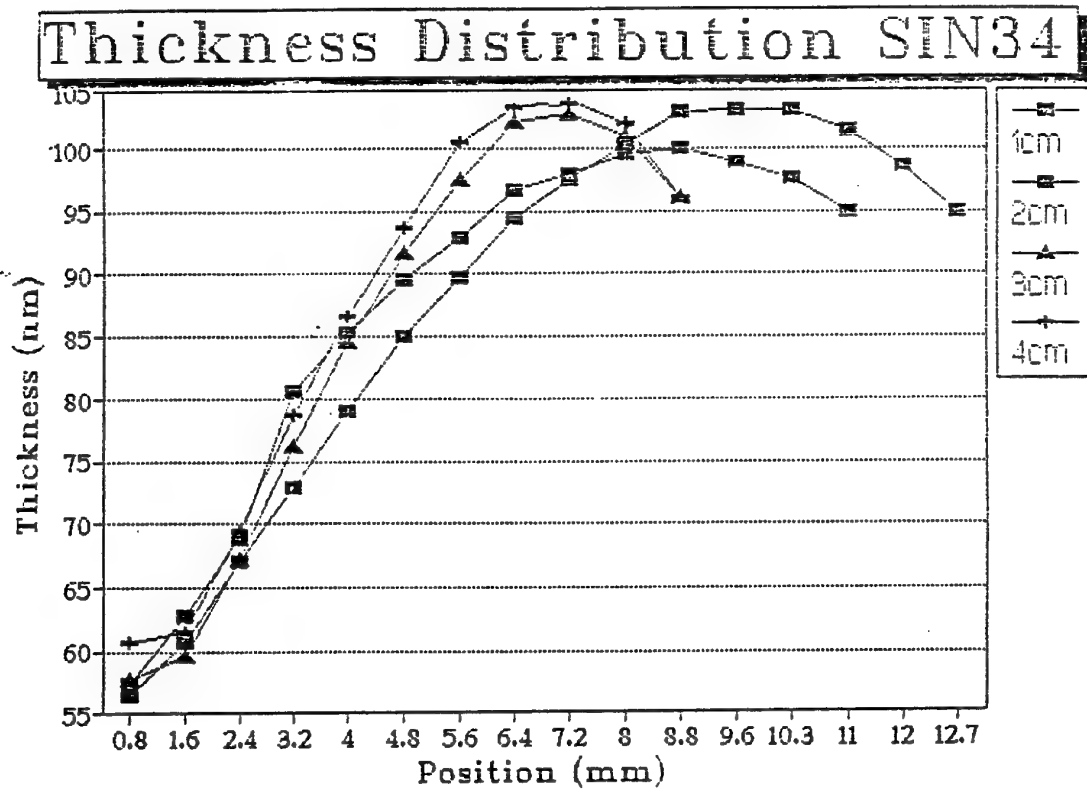


Fig 8: Transversal thickness distribution profile of silicon nitride films deposited at 250°C (run SIN34)

Fig.9 shows the refractive index distribution of the film deposited at 250°C. As was presented in figure 8 the four curves represent the transversal distribution along specimen width at four distances from the front edge of the specimen. The range of refractive index values is $n=2.1-2.22$. Generally looking at Fig. 8-9 and ignoring absolute values it can be seen that the shape of the refractive index curves can be correlated with the film thickness curves. The differences in the refractive indices along the specimen is unexpected and more work has to be done before coming to a conclusion.

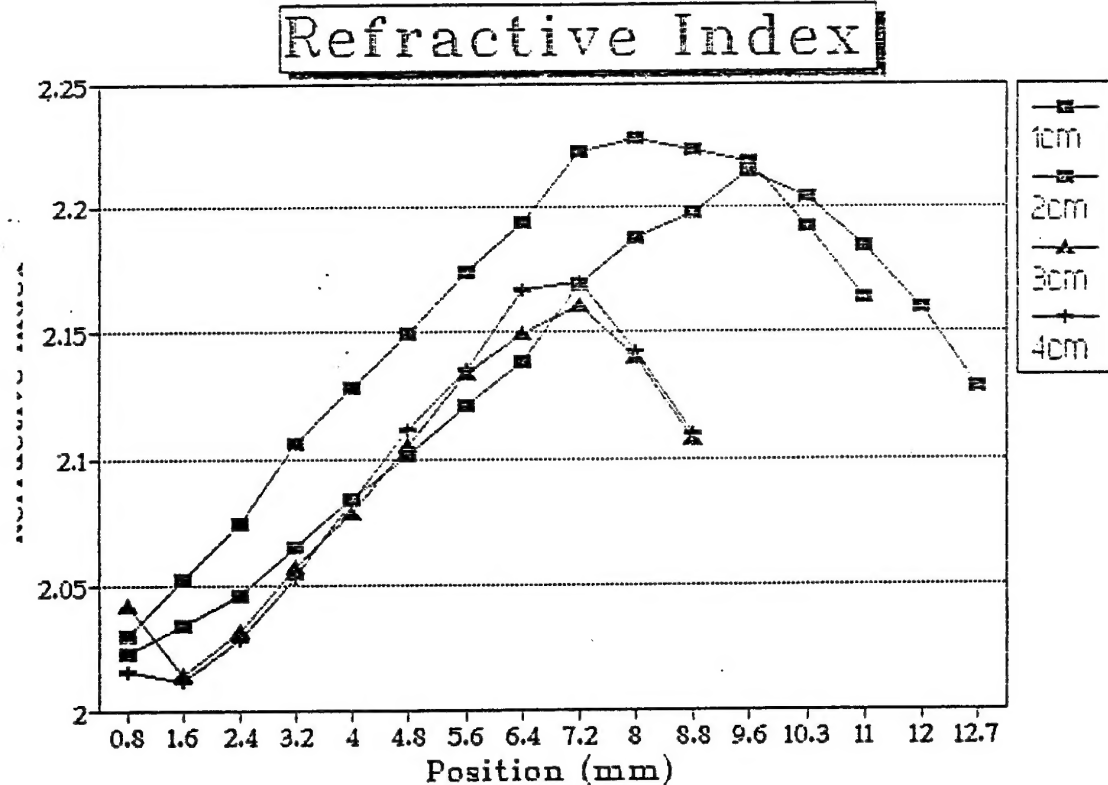


Fig 9: Transversal distribution profile of refractive index of silicon nitride films deposited at 250°C (run SIN34)

SUMMARY AND CONCLUSION

During this stage of the research it was shown that silicon films of good quality is possible at substrate temperature of 250°C. This temperature is not the limit value and further work will be done in order to lower the deposition temperature. It was found that powdered films were sometimes obtained and they contained high amount of oxygen. The source for the oxygen is not clearly understood, and is rather unexpected due to a high base vacuum of 10^{-6} Torr which is maintained in the chamber prior to deposition. This oxygen must be eliminated in following experiments.

The SI/N ratio was different at different substrate temperatures but no simple dependence can be found between them. A ratio of SI/N=1 was obtained at 400°C, SI/N=0.55 at 300°C and SI/N=0.8 at 250°C.

Refractive index of good quality films was $n=2.1-2.22$ at all temperatures and its value increased upon increasing film thickness.

Appendix C

NH2/SiH4/t.pressure.molecule		mass	16	17	18	20	28	29	30	31	32	40	NH/Total	SiH/total	NH/SiH
7.5/25	3.3		2.6E-09	5.6E-09		7.9E-08	4E-08	1.3E-07	1.3E-07	1E-07	9E-09	4E-07	0.0084868597	0.373693	0.022711
15/15	3.3		5.7E-09	1.8E-08		1.4E-07	1E-07	3.6E-07	3.6E-07	2.6E-07	2.3E-08	1.7E-04	0.0090919533	0.341851	0.026196
15/15-2			9E-09	3.1E-08		1.9E-07	1.7E-07	5.5E-07	5.5E-07	4.1E-07	3.3E-08	3.8E-06	0.0077026767	0.262565	0.029736
15/10	3.3		1.4E-08	5.6E-08		2.3E-07	1.8E-07	6.8E-07	6.8E-07	5.1E-07	4.4E-08	6.4E-06	0.008270643	0.204376	0.042212
15/10/10	5.9		1.1E-08	4.1E-08		2E-07	1.7E-07	5.7E-07	5.7E-07	4.4E-07	3.9E-08	9.3E-06	0.0048277783	0.132382	0.036459
15/7.5/1	5.9		1.3E-08	5.7E-08		1.4E-07	9E-08	3.4E-07	3.4E-07	2.7E-07	2.4E-08	1.2E-05	0.0054120922	0.067164	0.08058
#e11	0		5.3E-09	3.1E-08		1.4E-08	9E-09	0	0	4.5E-09	2E-10	1.5E-10	0.0206488676	0.134036	0.134035
25/15/50	4.8	4E-05	1.5E-08	4.1E-08		9E-08	8E-08	0	0	1.7E-07	1.6E-08	2.3E-06	0.2563458155	0.121325	2.112839
25/15/50	4.8	2.5E-05	2.3E-07	2.8E-07		5.5E-08	4.2E-08	0	0	7.5E-08	7.5E-09	1.3E-06			
#e12	0														
25/15/50	5.7	4E-05	1.7E-08	1.1E-07		3.9E-08	1.3E-08	2.3E-09	2.3E-09	1.3E-08	1.2E-09	1.4E-06	0.075988718	0.046466	1.706437
25/15/50	5.6	4E-05	2.3E-08	1.8E-07		5.9E-08	1.9E-08	5.2E-09	5.2E-09	1.5E-08	1.8E-09	3.4E-06	0.0548204159	0.028571	1.918715
25/15/50	5.4	3.6E-05	1.9E-08	1.4E-07		5.9E-08	1.4E-08	2.1E-09	2.1E-09	1E-08	1.1E-09	3.3E-06	0.048483738	0.025456	1.761821
25/15/50	5.2	3.6E-05	1E-07	2.5E-07		1E-07	1.8E-08	2.1E-09	2.1E-09	1.2E-08	1.4E-09	3.8E-06	0.0817088829	0.033939	2.407505
25/15/50	5	3.5E-05	3.1E-07	4.7E-07		1E-07	3E-08	2.3E-08	2.3E-08	2.9E-08	3E-09	3.4E-06		0.052133	0
#e18	0	3.3E-06	2.1E-08	1.4E-07	5.3E-07	7E-08	2.6E-08	2.7E-09	0	3.9E-09	0	2.2E-10	0.6377281376	0.317059	2.0113E7
15/9/100	5.957	3.7E-05	3.8E-08	2.7E-07	9.4E-07	1E-06	4.4E-08	3.6E-09	0	5.9E-09	0	2.4E-06	0.0655110071	0.012177	5.378462
15/9/100	5.9	3.7E-05	3.4E-08	2.1E-07	7.2E-07	9E-07	3.1E-08	2.9E-09	0	5.5E-09	0	2.2E-06	0.0593183255	0.010182	5.825541
15/9/100	5.8	3.5E-05	2.4E-08	1.1E-07	3.1E-07	3.3E-07	1.7E-08	2.5E-09	0	3.9E-09	0	1.1E-06	0.0704229577	0.01327	5.322074
15/9/100	5.7	3.4E-05	2.1E-08	1E-07	3.1E-07	3.4E-07	1.9E-08	3.7E-10	0	3.8E-09	0	1.2E-06	0.0653571945	0.012475	5.259119
15/9/100	5.66	3.4E-05	4.2E-08	1.6E-07	4.9E-07	5E-07	3.2E-08	4.9E-10	0	3.7E-09	0	1.7E-06	0.045585051	0.01374	3.27017
15/9/100	5.62	3.5E-05	4E-08	1.4E-07	3.7E-07	6.4E-07	4.3E-08	5.9E-10	0	5.4E-09	0	2.1E-06	0.0576979654	0.01485	3.885383
15/9/100	5.53	3.2E-05	6.5E-08	1.8E-07	4.2E-07	5.2E-07	3.80E-08	4.30E-10	0.00E+00	5.10E-09	0.00E+00	1.7E-06	0.0639763704	0.016529	3.870531
15/9/100	5.39	3E-05	7.8E-08	1.7E-07	3.2E-07	6.6E-07	4.1E-08	4.7E-10	0	5.4E-09	0	2E-06	0.072699978	0.014989	4.847414
15/9/100	5.63	3.4E-05	6.8E-08	1.4E-07	2.2E-07	5.1E-07	3.7E-08	5.7E-09	0	1.2E-08	0	1.6E-06	0.0907626995	0.021897	4.145082
15/9/100	5.65		8.8E-08	1.6E-07	2.4E-07	3.8E-07	2.2E-08	8.1E-09	0	1E-08	0	1.2E-06	0.102058363	0.016447	6.205063
15/9/100						4.2E-07	2.7E-08	1.3E-08	0	1.9E-08	0	1.3E-06	0.1093956771	0.029222	3.743557
SiH40			1.2E-08	8E-09		4.9E-08	5.3E-10		0	7E-09	3.7E-10	4.3E-06	0.0045694441	0.01306	0.349886
25/15/50		7E-05	2.5E-08	2.9E-08		5.4E-08	3.8E-10		0	6E-09	4.3E-10	4.6E-06	0.0114532717	0.013047	0.877841
SiH39															
25/15/50	5.4	1.9E-05 before 10K	4.8E-09	1.8E-08		2E-08	3.2E-10		0	4.7E-09	2.9E-10	1.3E-06	0.0169125663	0.019097	0.885594
			5E-09	2.1E-08		2.4E-08	5.2E-10		0	4.8E-09	2.5E-10	1.8E-06	0.014011867	0.016162	0.866545